

## CHAPTER IV

### RESULTS AND DISCUSSION

The influence of carbon black type and loading on reversion behavior and thermal aging properties of natural rubber (NR) compounds was focused in this study. To make it clearer and easier to understand, the results and discussion were divided into two parts. For the first part, most attention was only paid to the cure characteristics, reversion behavior, and thermal aging properties of the gum or unfilled NR compound. And then, how the presence of carbon black effected on those properties of NR compounds was discussed regarding to carbon black type and carbon black loading.

#### 4.1 Cure Characteristics, Reversion Behavior and Thermal Aging Properties of Gum NR Compound

In this part, the changes in the cure characteristics, reversion behavior, and thermal aging properties of the gum NR compound cured with DCBS-accelerated sulfur system as a function of the curing conditions including curing temperature and curing time were discussed.

##### 4.1.1 Cure Characteristics of Gum NR Compound

The cure curves showing the time dependence behavior of torque of the gum NR compound at the different curing temperatures of 130, 140, 150, 160, 170, and 180°C are depicted in Figure 4.1.

From Figure 4.1, it was clearly observed that the cure characteristics of the gum NR compound depended significantly on the curing temperature. All important cure characteristics including minimum torque ( $M_l$ ), maximum torque ( $M_H$ ), scorch time ( $ts_2$ ), 90% of cure time ( $tc_{90}$ ), 100% of cure time ( $tc_{100}$ ) and cure rate index (CRI) of the gum NR compound cured at different curing temperatures are deducted from Figure 4.1 and given in Table 4.1.

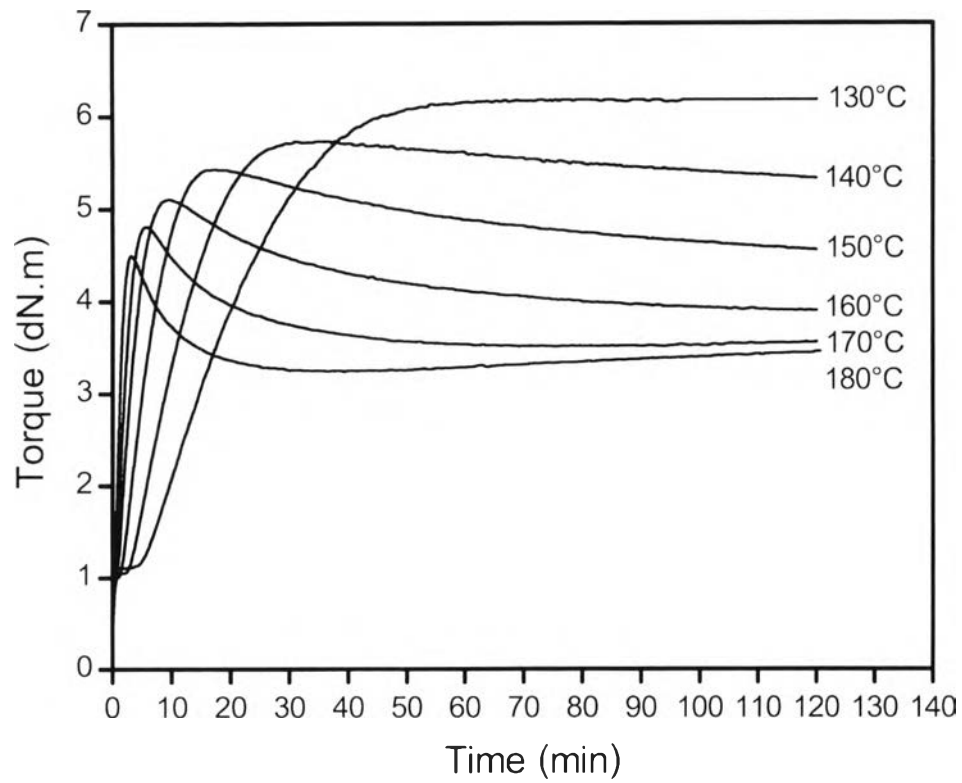


Figure 4.1 Cure curves of gum NR compound at different curing temperatures

Table 4.1 Cure characteristics of gum NR compound at different curing temperatures

Curing temperature	$M_L$ (dN.m)	$M_H$ (dN.m)	$M_H - M_L$ (dN.m)	$ts_2$ (min)	$tc_{90}$ (min)	$tc_{100}$ (min)	CRI
130°C	1.07	6.17	5.10	15.0	37.0	66.6	4.55
140°C	1.05	5.74	4.69	9.07	20.3	38.0	8.90
150°C	1.00	5.43	4.43	5.07	11.1	17.3	16.7
160°C	0.94	5.11	4.17	2.56	6.07	9.30	28.5
170°C	1.19	4.82	3.63	2.12	3.48	6.05	73.5
180°C	1.09	4.51	3.42	1.19	2.09	3.00	111

The scorch time, cure time and cure rate index were plotted against the curing temperature as shown in Figure 4.2. It can be seen that the curing reaction was accelerated by increasing in the curing temperatures, thus leading to the lowering of both scorch time and cure times ( $tc_{90}$  and  $tc_{100}$ ). The cure rate index increased significantly when the curing temperature was increased from 130 to 180°C as shown in Figure 4.2. The increase in the curing temperatures seemed to have only slightly effect on the minimum torque ( $M_c$ ). However, the increase in the curing temperatures caused the maximum torque ( $M_H$ ) to decrease noticeably. It is known that for the unfilled rubber compound, the maximum torque ( $M_H$ ) is related directly to the number of crosslink formed. The higher the maximum torque ( $M_H$ ) value, the higher the formation of crosslink. So the result here showed that although the curing reaction could be completed within the shorter time when using higher curing temperature, the obtained network was formed by the less crosslink points. The use of high curing temperature led to the reduction of crosslink points as shown in Figure 4.1. Therefore, the curing temperature must be compromised.

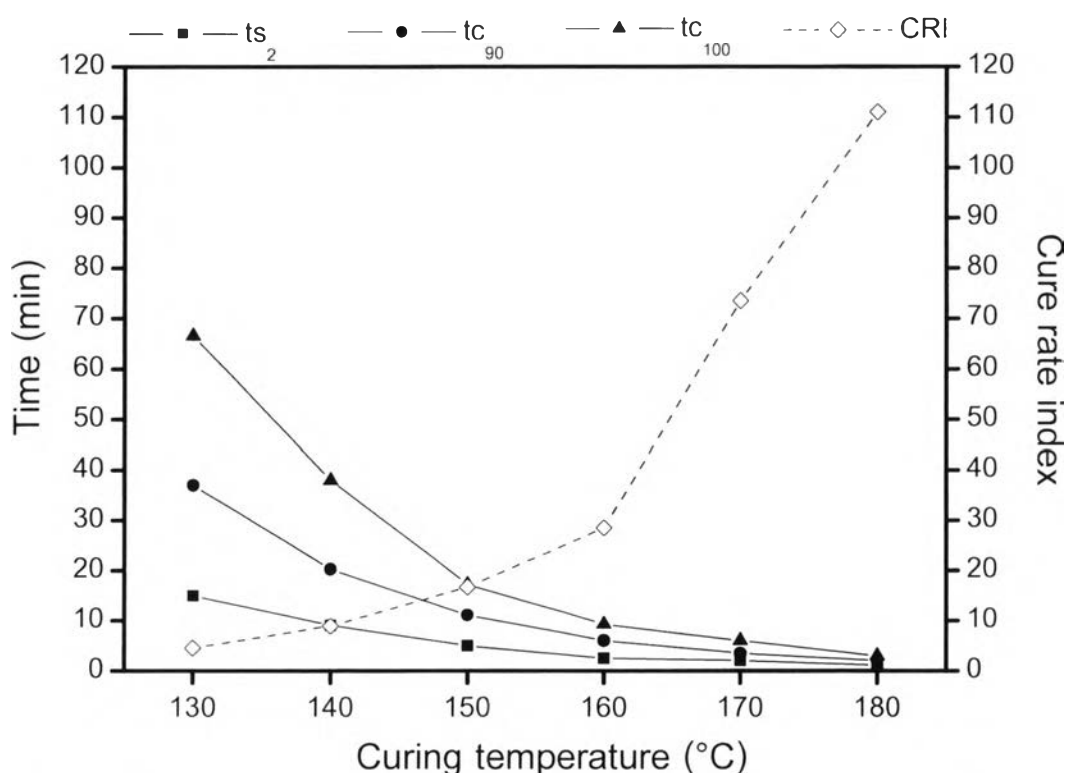


Figure 4.2 Scorch time ( $ts_2$ ), cure time ( $tc_{90}$  and  $tc_{100}$ ) and cure rate index (CRI) of gum NR compound at different curing temperatures

The effect of the curing temperature on the crosslinking degree was also studied intensively by Loo [63]. The result from this work was comparative to the result from Loo's work. To make it easier to understand what caused this phenomenon, it was better to start the discussion from the mechanism of the accelerated sulfur vulcanization.

Krejsa and Koenig [64] proposed that the mechanism of the accelerated sulfur vulcanization is consisted of three major steps. The reaction starts from the formation of the active sulfuration agents. Next is the formation of crosslinking, which includes the formation of accelerated-terminated polysulfidic pendent groups as the rubber bound precursors and the formation of crosslinks. So in this step, the initially formed crosslinks are mainly polysulfide. The last step is the post-crosslink reaction or maturing reaction consisting of two competitive reactions. The first reaction is desulfuration of polysulfidic crosslinks to form the shorter crosslinks. And the sulfurs removed from the polysulfides are able to sulfurate more rubber chains to form the additional crosslinks. The second reaction is decomposition of polysulfidic crosslinks, forming cyclic sulfides, conjugated dienes in the rubber back bone, and zinc sulfide. Therefore the decomposition leads to the loss of net crosslinks. Loo [63] proposed that a reduction in crosslink density at higher curing temperatures is because fewer polysulfidic crosslinks are initially formed owing to fewer effective sulfuration agents being available. Moreover, it was also proposed that at high curing temperature, polysulfidic crosslinks formed initially can undergo desulfuration slowly, thus resulting in the crosslinks of higher sulfur ranks. Since thermal instability increases with the number of sulfur atoms in the crosslinks, such these crosslinks are very susceptible to thermal decomposition. This leads to the formation of cyclic sulfide, conjugated dienes and zinc sulfide. These are the reasons why the lower crosslinks will be observed at the higher curing temperatures.

#### 4.1.2 Reversion Behavior of Gum NR Compound

The reversion behavior can be observed from cure curve when torque decreases after reaching maximum. From Figure 4.1, it was observed that the gum NR compound was reversion free when the curing temperature was not higher than 130°C. For the particular curing system used in this study, the reversion of gum NR compound was initially observed

at the curing temperature of 140°C. Reversion behavior was indicated here by two parameters which can be taken from the cure curve. The first parameter was the range of the plateau region after torque reaching maximum. This parameter was relevant to the thermal stability of the obtained networks. The second parameter was the slope of the decreasing torque at the prolonged cure stage. This slope represented the reversion rate. The effect of the curing temperature on both parameters is shown in Figure 4.3.

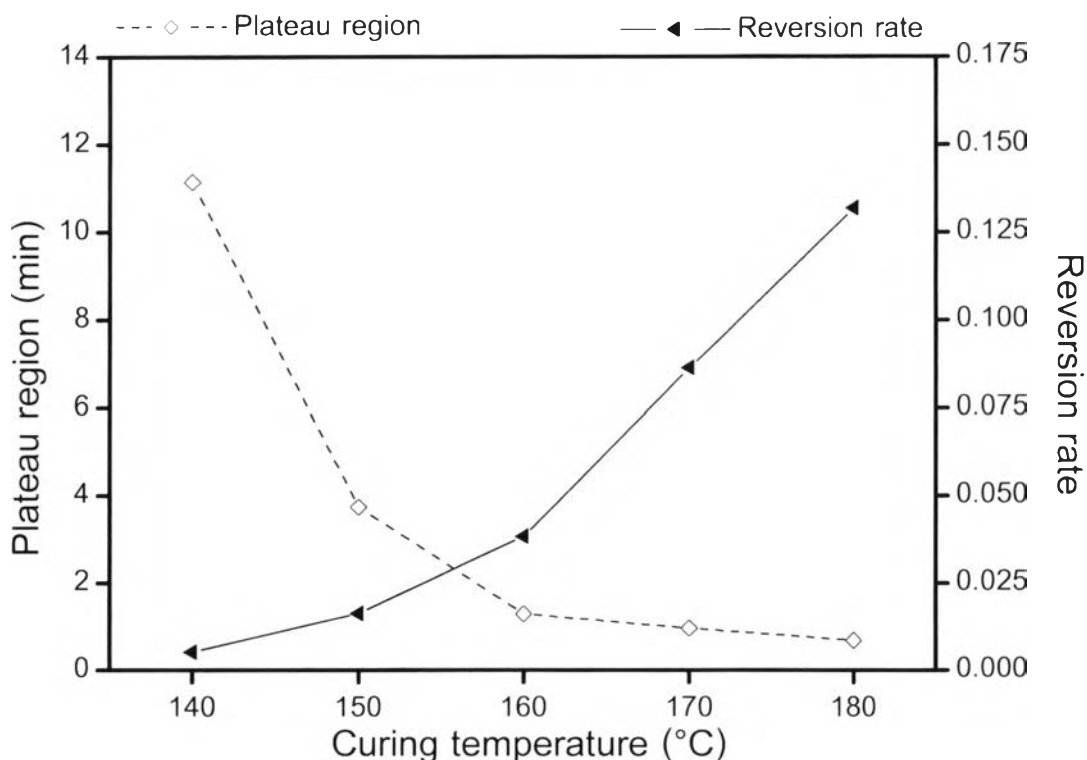


Figure 4.3 Plateau region and reversion rate of gum NR compound at different curing temperatures

From Figure 4.3, it was observed that the increasing of curing temperatures led to the shorter plateau region and the faster reversion rate. This indicated that the networks obtained at the high curing temperatures had less thermal stability. As mentioned earlier, the obtained networks formed at the high curing temperature consist of polysulfidic crosslinks with higher sulfur ranks. Due to their lower bond energy, therefore, the opportunities to decompose of polysulfidic crosslinks at the prolonged cure stage should increase and then reversion rate also increased at the high curing temperature circumstance.

#### 4.1.3 Thermal Aging Properties of Gum NR Compound

Thermal aging properties of the gum NR compound cured at 160°C with various curing times including the 90% cure time ( $t_{c_{90}}$ ), the 100% cure time ( $t_{c_{100}}$ ) and the 20 min above 100% cure time ( $t_{c_{100+20\text{ min}}}$ ) were discussed in this part. The 100% modulus (M100), % elongation at break (EB) and tensile strength (TS) of the gum NR compound before and after thermal aging and their relative M100, relative EB and relative TS were compared in Figures 4.4-4.6.

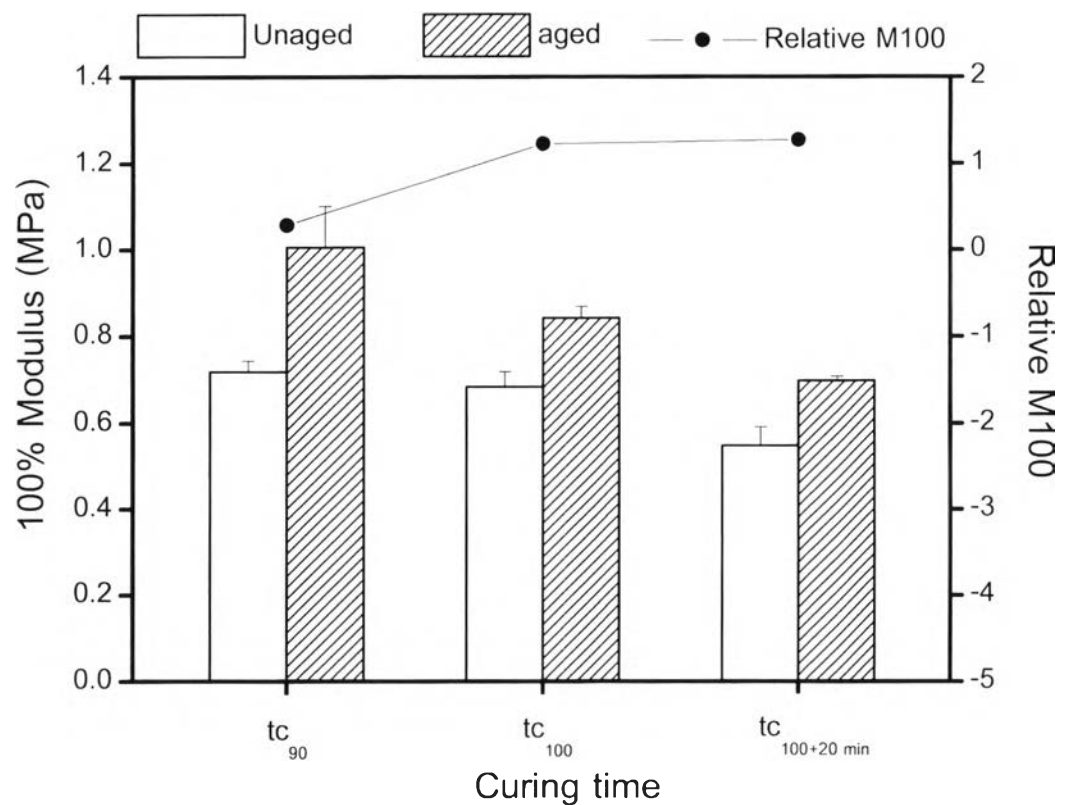


Figure 4.4 100% modulus (M100) before and after thermal aging and their relative values of gum NR compound cured at 160°C with different curing times

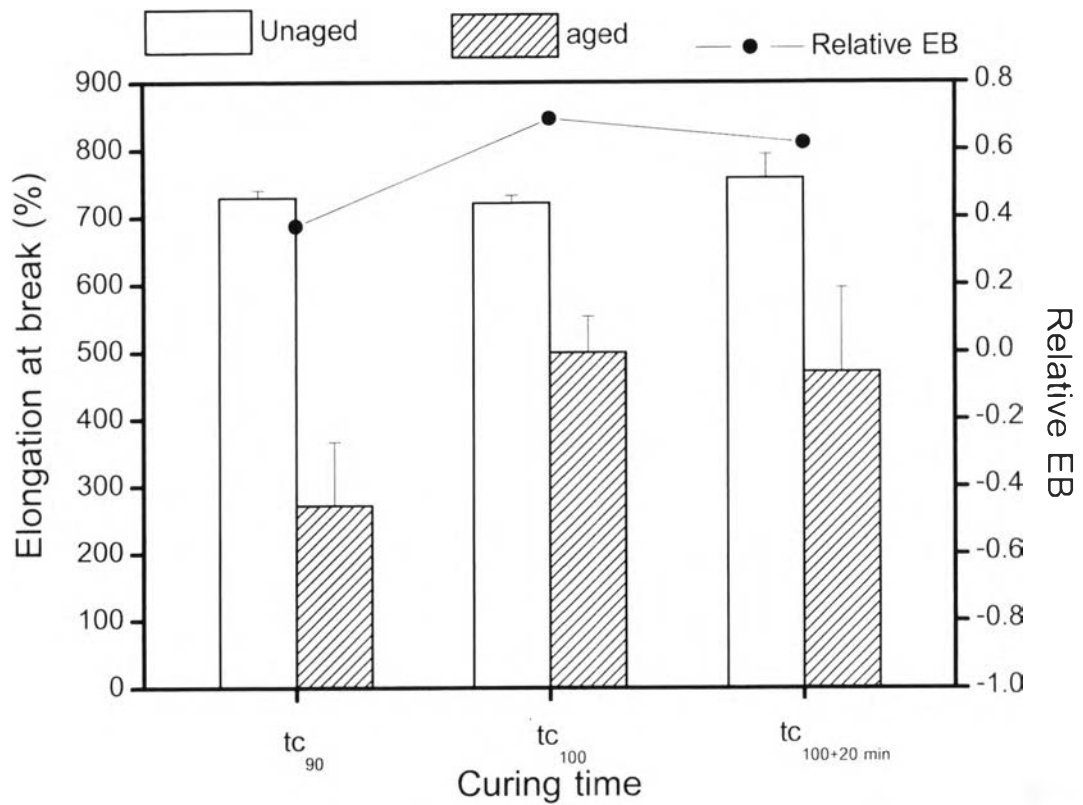


Figure 4.5 %Elongation at break (EB) before and after thermal aging, and their relative values of gum NR compound cured at  $160^{\circ}\text{C}$  with different curing times

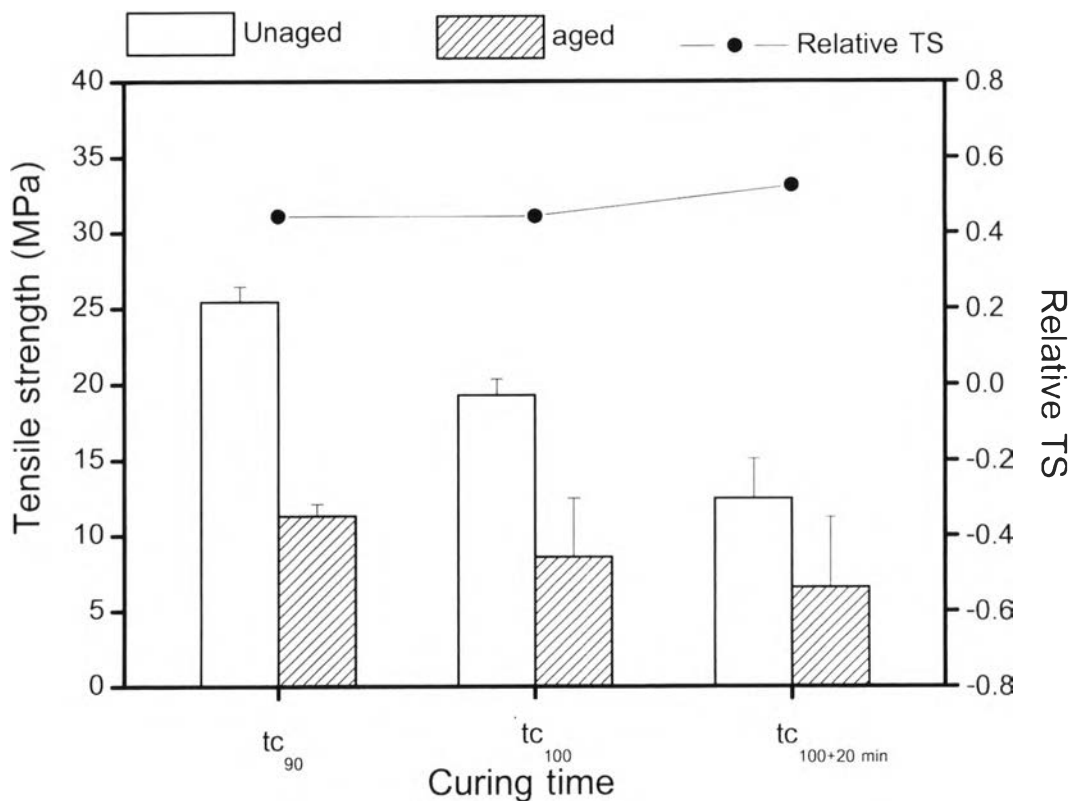


Figure 4.6 Tensile strength (TS) before and after thermal aging, and their relative values of gum NR compound cured at  $160^{\circ}\text{C}$  with different curing times

It can be seen that after thermal aging the 100% modulus of the three gum NR specimens cured with different curing times increased all. The relative M100 of the gum NR specimen cured with  $tc_{90}$  was lower than that of the other two cured with  $tc_{100}$  and  $tc_{100+20 \text{ min}}$ . The increase in modulus implied that the aged specimens had the higher crosslink densities. And this can be supported by the increase of crosslink density determined from the swelling method as shown in Figure 4.7. The increase in the crosslink density after aging reduced the mobility of the rubber chains. As a consequence, the aged specimens could be extended less, thus resulting in having lower %elongation at break. Figure 4.6 represents the tensile strength before and after thermal aging as well as the relative TS of gum NR specimens cured with various curing times. It can be seen that the tensile strength of all gum NR specimens tended to decrease after exposing to the heat. This may be because the degree of crosslinking after aging exceeded the optimum value and the networks became too dense, leading to the decrease in tensile strength [65-67]. It was apparent that the relative TS of all gum NR specimens cured with different curing times were not much different.

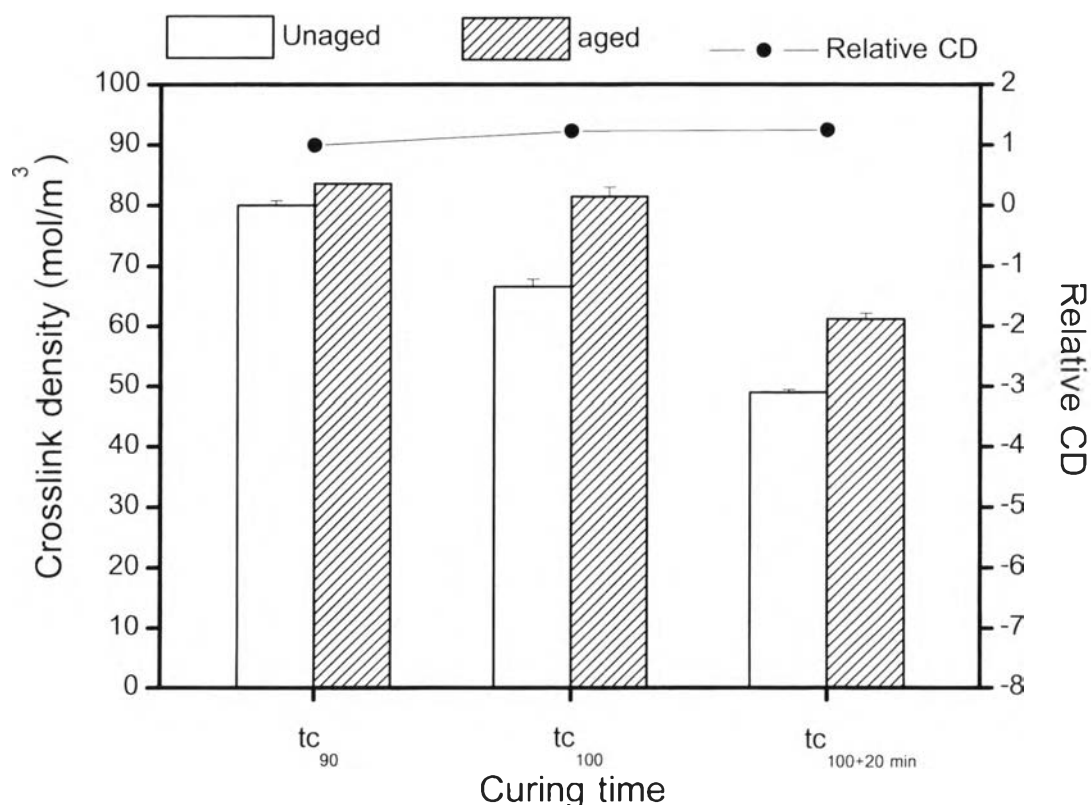


Figure 4.7 Crosslink density (CD) before and after thermal aging, and their relative values of gum NR compound cured at 160°C with different curing times



Result presented in Figure 4.7 was worth to comment one thing about the optimum curing time. It can be seen that the specimen cured with  $t_{c_{90}}$  had higher crosslink density than the one cured with  $t_{c_{100}}$  even the results from the cure curves indicates that the degree of crosslink at  $t_{c_{90}}$  stage was lower than that at  $t_{c_{100}}$  stage. It is well known that rubber has low heat conductivity. Therefore, after taking rubber out from the heating mold, if there is no instantaneous cooling, the curing reaction still continues. If rubber compound had high reversion resistance, curing with either  $t_{c_{90}}$  or  $t_{c_{100}}$  will not show any much difference in crosslink density. However, if rubber compound is prone to undergo reversion at the prolonged cure stage, vulcanizate taking out at  $t_{c_{100}}$  without any instantaneous cooling will absolutely undergo reversion process, thus resulting in having lower crosslink density. Therefore, the  $t_{c_{90}}$  is considered to be the optimal curing time for the rubber curing as overheating the rubber could lead to reversion process.

#### 4.2 Influence of Carbon Black on Cure Characteristics, Reversion Behavior and Thermal Aging Properties of NR Compounds

Rubber must be reinforced with fillers such as carbon black and silica to improve the end-use performance along with the increased in modulus and ultimate properties. However, the consequences of incorporation of them on the reversion behavior and thermal aging properties of rubber compounds seem to be scarce. The study here was only focused on the carbon black filled NR compounds. In this part, the effects of carbon black type and loading on the cure characteristics, reversion behavior and thermal aging properties of the NR compounds were investigated using four types of carbon black (N330, N550, N776, and N990, which are different in primary size and structure). The carbon black loading was varied from 10 to 50 phr with the increments of 10 phr.

#### 4.2.1 Cure Characteristics of Carbon Black Filled NR Compounds

The study in this part was divided into four parts. The first part was focused on the cure characteristics of the carbon black filled NR compounds cured at the different curing temperatures. Then the rests were focused on the effect of type, loading and surface activity of carbon black on the cure characteristics of NR compounds.

##### 4.2.1.1 Effect of curing temperature on cure characteristics of NR compounds

As seen in the previous result, the curing temperature played an important role on the cure characteristics of the gum NR compound. So here the effect of the curing temperature on the cure characteristics of the carbon black filled NR compounds was first focused. The carbon black loading was fixed at 50 phr. The cure curves at different curing temperatures of N330, N550, N776 and N990 filled NR compounds are shown in Figure 4.8.

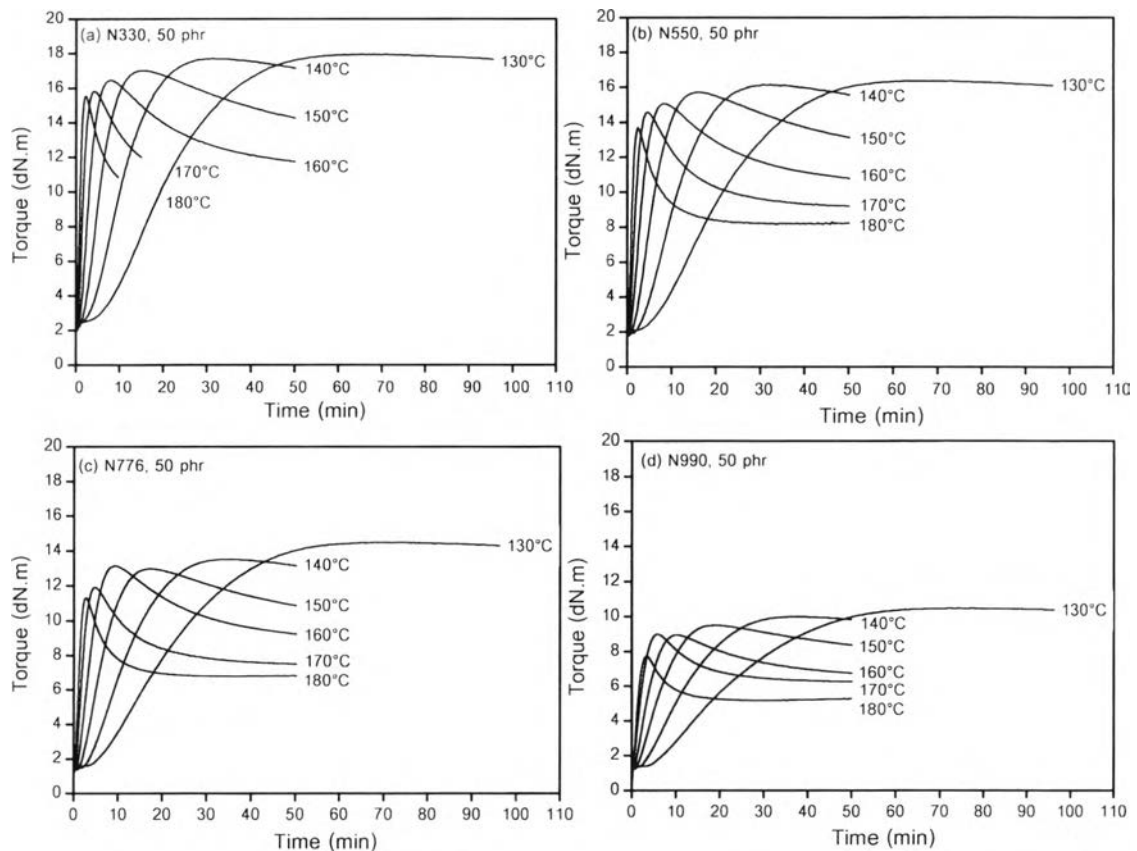


Figure 4.8 Cure curves at different curing temperatures of (a) N330, (b) N550, (c) N776 and (d) N990 filled of NR compounds

From Figure 4.8, it was clearly observed that the cure characteristic of N330, N550, N776 and N990 filled NR compound also depended significantly on the curing temperatures. All important cure characteristics including minimum torque ( $M_L$ ), maximum torque ( $M_H$ ), scorch time ( $ts_2$ ), 90% of cure time ( $tc_{90}$ ), 100% of cure time ( $tc_{100}$ ) and cure rate index (CRI) of NR compounds cured at different curing temperatures are deducted from Figure 4.8 and given in Tables 4.2-4.5, respectively.

Table 4.2 Cure characteristics at different curing temperatures of NR compounds filled with 50 phr of N330

Curing temperature	$M_L$ (dN.m)	$M_H$ (dN.m)	$M_H - M_L$ (dN.m)	$ts_2$ (min)	$tc_{90}$ (min)	$tc_{100}$ (min)	CRI
130°C	2.50	18.0	15.5	8.01	38.5	68.0	3.28
140°C	2.31	17.7	15.4	4.54	19.2	31.2	6.81
150°C	2.17	17.0	14.8	2.38	9.44	15.3	14.2
160°C	2.02	16.5	14.5	1.26	5.09	8.06	26.1
170°C	2.05	15.8	13.8	0.49	2.45	4.09	51.0
180°C	2.11	15.5	13.4	0.33	1.31	2.16	102

Table 4.3 Cure characteristics at different curing temperatures of NR compounds filled with 50 phr of N550

Curing temperature	$M_L$ (dN.m)	$M_H$ (dN.m)	$M_H-M_L$ (dN.m)	$ts_2$ (min)	$tc_{90}$ (min)	$tc_{100}$ (min)	CRI
130°C	2.11	16.4	14.3	9.28	39.3	66.5	3.33
140°C	1.94	16.2	14.3	5.01	20.0	30.3	6.66
150°C	1.85	15.7	13.9	2.37	10.2	16.2	12.8
160°C	1.78	15.1	13.3	1.26	5.25	8.27	25.1
170°C	1.88	14.6	12.7	0.53	3.02	4.24	40.2
180°C	1.81	13.7	11.9	0.34	1.39	2.21	95.2

Table 4.4 Cure characteristics at different curing temperatures of NR compounds filled with 50 phr of N776

Curing temperature	$M_L$ (dN.m)	$M_H$ (dN.m)	$M_H-M_L$ (dN.m)	$ts_2$ (min)	$tc_{90}$ (min)	$tc_{100}$ (min)	CRI
130°C	1.57	14.5	12.9	10.1	41.7	73.6	3.19
140°C	1.48	13.5	12.0	5.52	22.0	35.1	6.06
150°C	1.37	13.0	11.6	3.07	11.2	17.2	12.3
160°C	1.41	13.1	11.7	1.47	6.13	9.15	21.7
170°C	1.30	11.9	10.6	0.58	3.11	4.51	39.5
180°C	1.30	11.3	10.0	0.39	1.51	2.39	89.3

**Table 4.5** Cure characteristics at different curing temperatures of NR compounds filled with 50 phr of N990

Curing temperature	$M_L$ (dN.m)	$M_H$ (dN.m)	$M_H-M_L$ (dN.m)	$ts_2$ (min)	$tc_{90}$ (min)	$tc_{100}$ (min)	CRI
130°C	1.38	10.5	9.12	11.6	44.3	74.5	3.06
140°C	1.35	10.0	8.65	6.38	23.3	35.5	5.90
150°C	1.22	9.51	8.29	3.28	12.2	18.4	11.3
160°C	1.24	8.96	7.72	2.04	6.47	9.54	22.6
170°C	1.39	8.99	7.60	1.10	3.53	5.43	41.2
180°C	1.41	7.73	6.32	0.53	2.17	3.18	61.0

It can be seen the effect of the increasing curing temperature on the cure characteristics of NR compounds seemed to be the similar trend for all types of carbon black. As can be seen in Tables 4.2-4.5, the increase in the curing temperature accelerated the curing reaction, thus lowering the scorch time ( $ts_2$ ) and cure times ( $tc_{90}$  and  $tc_{100}$ ) but increasing the cure rate index (CRI). The increase in the curing temperature caused the reduction of the minimum torque ( $M_L$ ) and the maximum torque ( $M_H$ ). As mentioned previously by Loo [63], the higher curing temperatures led to fewer available effective sulfuration agents and slower desulfuration rate and hence the value of the maximum torque ( $M_H$ ) relating to the degree of crosslink density would decrease. This phenomenon also occurred with the gum NR compound as shown in the previous part (4.1.1).

#### 4.2.1.2 Effect of carbon black type on cure characteristics of NR compounds

There were four different carbon black types used here including N330, N550, N776 and N990. The first three are produced by the same incomplete combustion process and called as furnace black. The differences amongst these three carbon blacks are the surface area and the degree of structure as shown in Table 3.2. N330 has the highest surface area with medium structure. N550 has the highest structure but its surface area is lower than that of N330. Compared to N330 and N550, N776 has the lowest surface and structure. N990 is produced by thermal cracking process and called as thermal black. Compared to the previous three carbon blacks, N990 has the lowest surface area and structure. In addition to the physical properties of carbon black, other factors that can affect the cure system include the pH of the carbon black, ash, and sulfur level on the carbon black surface. There were two points to discuss here. The first one was how the presence of carbon black altered the cure characteristics of the NR compound when compared to that of the gum NR. Then for any change in the cure characteristics including the scorch time ( $t_{s_2}$ ), 90% cure time, ( $t_{c_{90}}$ ) and cure rate index (CRI) due to the presence of carbon black, how this related to the carbon black type. The carbon black loading was fixed at 50 phr. The results are given in Figures 4.9-4.11.

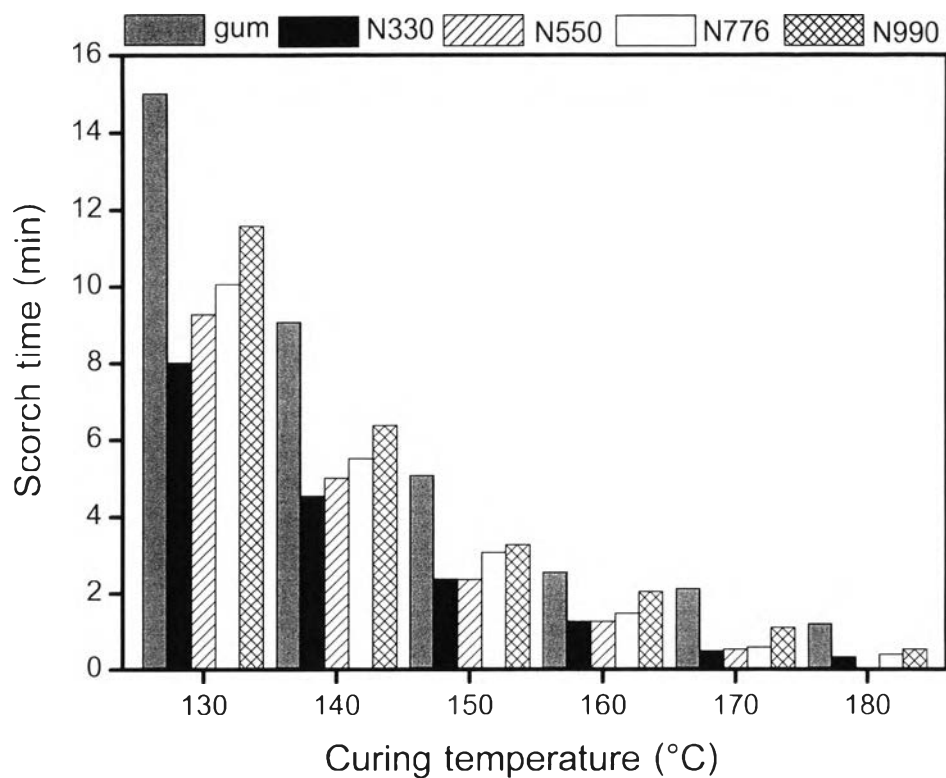


Figure 4.9 Scorch times at different curing temperatures of gum and various carbon black types filled NR compounds

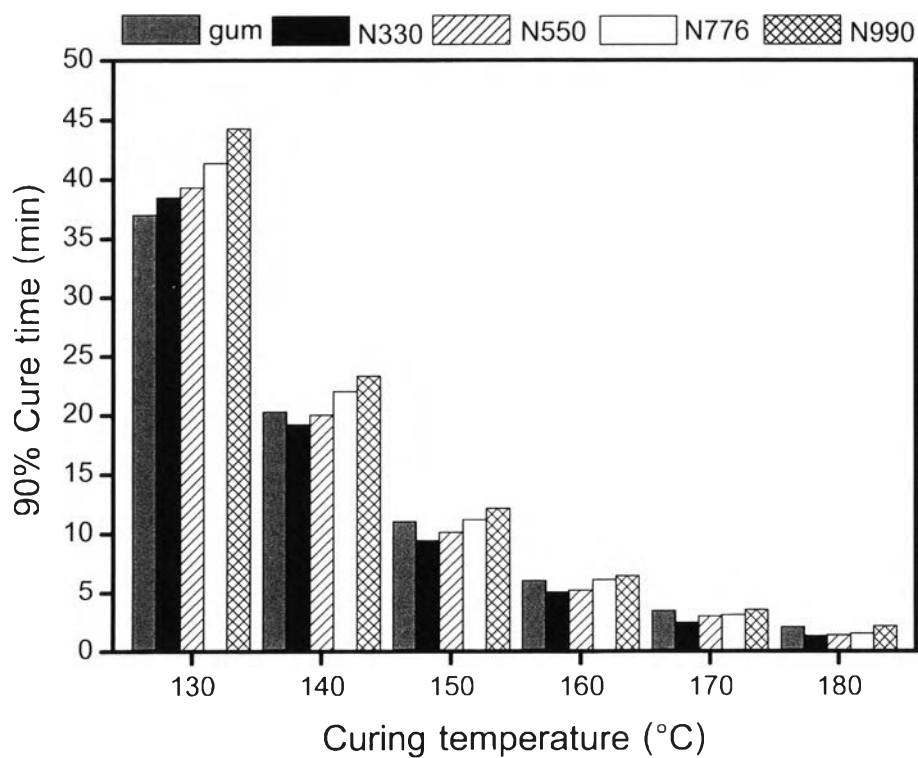


Figure 4.10 90% cure times at different curing temperatures of gum and various carbon black types filled NR compounds

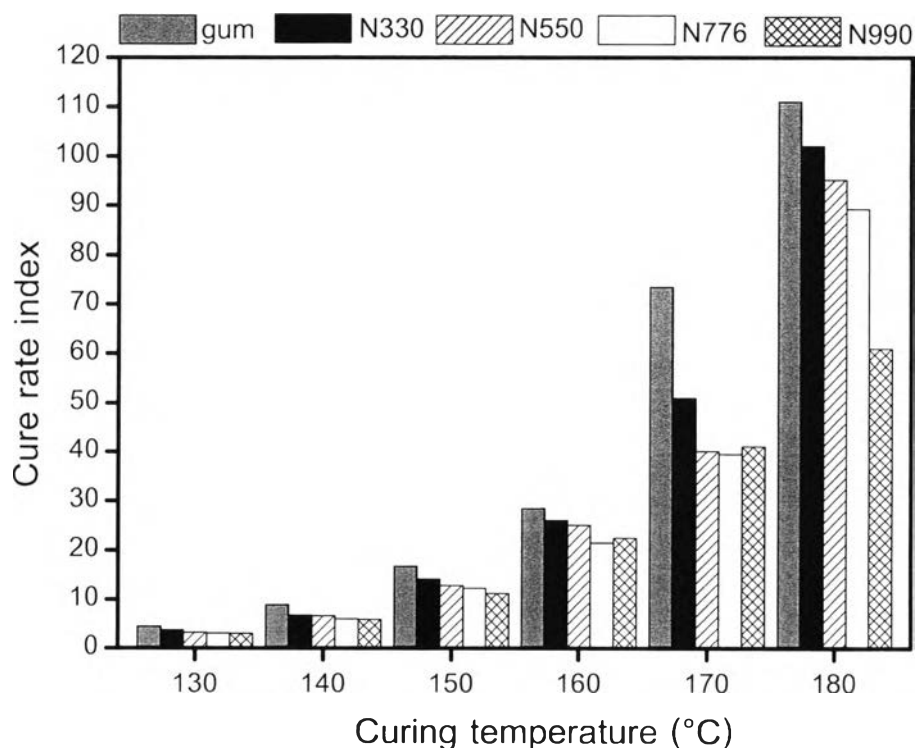


Figure 4.11 Cure rate indices at different curing temperatures of gum and various carbon black types filled NR compounds

Shown in Figure 4.9 is a plot of the scorch time at different curing temperatures of gum and various carbon black type filled NR compounds. It can be seen that no matter which curing temperature the presence of carbon black decreased the scorch time. Studebaker proposed that there are two reasons for this behavior [2]. With delayed action accelerators of the sulfenamide type, it is necessary to break the S-N bond before the accelerator becomes active. Carbon black catalytically promotes the rupture of the S-N linkages when heated. Second, most sulfur-containing vulcanizing systems can be activated by trace amounts of hydrogen sulfide. Carbon black promotes the formation of hydrogen sulfide. So this can lead to the shorter scorch time. In addition, it was also observed the reduction of the scorch time was carbon black type dependent. The reduction of the scorch time seemed to be the inversely order with the carbon black surface area. Therefore, it was most-marked for the addition of N330.



Figure 4.10 shows the 90% cure time at different curing temperatures of gum and various carbon black type filled NR compounds. Compared to the gum NR compound, for all curing temperatures except 130°C, the presence of N330 and N550 reduced the 90% cure time. On the other hand, the addition of N776 and N990 decreased the 90% cure time when compared to the gum NR compound only above 170°C. The effect of the carbon black types on the cure time had been studied extensively [66]. It was found that the cure time was influenced by the combination of structure and surface area of the carbon black. The latter factor also directly relates to many factors including the functional group and the sulfur content on the carbon black surface. It was reported that furnace blacks have a neutral or slightly alkali pH with low oxygen content which has accelerating effect on the cure characteristics of rubber [66]. Between two furnace blacks, N550 and N330, Choi and coworker [66] found that the cure time and cure rate of the compound filled with N550 was faster than those of the compound filled with N330. It was proposed that the compound filled with the higher structure carbon black, N550, had more the tightly bound rubber than the one filled with the lower structure carbon black, N330. The tightly bound rubber in the immediate vicinity of the carbon black was likely to impede the curative adsorption on the filler surface. The effective prevention of curative adsorption allowed more free curatives to be available in the rubber matrix, and then the crosslinking reactions became faster. Moreover, Li and coworkers [69] studying the effect of the carbon black type on the vulcanization characteristics found that amongst the carbon blacks under their study including N330, N472, N550, N770 and SCB (spraying carbon black), the compound filled with N472 had the shortest cure time. The explanation given was about the amount of sulfur at the carbon black surface. As mentioned earlier, carbon black is produced from the petroleum or natural gas. Therefore, besides carbon, there is a trace amount of sulfur at the surface which can involve in the sulfur vulcanization. In general, furnace black has the higher sulfur level than thermal black. And amongst furnace blacks, the content of sulfur is highly associated with the surface area of carbon black. Li and coworkers [69] showed that N472 having the largest

surface area had the highest sulfur content. This was the reason why the compound filled with N472 had the shortest cure time. However, it was pointed out by the authors that considering the difference in the surface area and sulfur content between N330 and N550, the degree of the decreased cure time for the N330-filled compound was not much higher than that of the N550 filled one. N330 was the exception because the phenolic group found only on N330 can reduce the crosslinking efficiency. Due to the absence of sulfur on the surface of N770, the compound vulcanized without the influence of sulfur on the carbon black surface, resulting in having the longest cure time.

According to above literatures, it might be the sulfur at the carbon black surface and its surface activity that caused the NR compound filled N330 in having the shortest cure time. Compared to the gum NR compound, the incorporation of N776 and N990 into NR compounds caused the longer cure times. This might not be only the absence of the sulfur on the carbon black surface but also the curative adsorption on the carbon black surface.

Figure 4.11 shows the cure rate index at different curing temperatures of gum and various carbon black type filled NR compounds. It was observed that at every curing temperature used here, the gum NR compound clearly showed the higher overall vulcanization rate compared to NR compounds filled with carbon black. According to ASTM standard mentioned in Chapter III, cure rate index is a measurement of vulcanization rate based on the difference between optimum vulcanization and incipient scorch time, at which vulcanization begins. As seen in Figure 4.10, the presence of carbon black no matter which carbon black type caused the NR compound cured at 130°C in having the longer 90% cure time and the shorter scorch time. Therefore, it was inevitable for carbon black filled NR compounds cured at 130°C to have the slower cure rate than the gum NR compound. However, at the curing temperatures above 130°C, the shorter 90% cure time of NR filled with N330 compared to that of the gum one still resulted in the slower cure rate. This might be due to the connection between the reduction of the 90% cure time with respect to that of the scorch time. The reduction of the

scorch time may not be enough to result in the increase of the cure rate. Comparison between different carbon black types, no matter which curing temperature, the NR compound filled with N330 showed the faster cure rate than the NR compound filled with other carbon blacks. The ability to speed up the curing reaction of N330 over other three carbon blacks was maximized at the higher curing temperature as shown in Figure 4.11.

#### 4.2.1.3 Effect of carbon black loading on cure characteristics of NR compounds

From the previous part, it was found that the incorporation of carbon black 50 phr into the NR compound resulted in the different cure characteristics comparing with the gum one. In this part, the changes in the cure characteristics of the NR compounds when the carbon black loading was consecutively increased were determined. The curing temperature was fixed at 160°C.

The cure curves showing the time dependence behavior of torque of the carbon black filled NR compounds cured at 160°C are depicted in Figure 4.12.

It can be seen in Figure 4.12 that for all carbon black types, the cure characteristics were carbon black dose dependent. The cure characteristics of the NR compounds filled with N990 showed the least carbon black dose dependent. The cure characteristics at 160°C of N330, N550, N776 and N990 filled NR compounds with various carbon black loadings including the minimum torque ( $M_l$ ), maximum torque ( $M_H$ ), scorch time ( $t_{s_2}$ ), 90% of cure time ( $t_{c_{90}}$ ), 100% of cure time ( $t_{c_{100}}$ ) and cure rate index (CRI) from Figure 4.12 are summarized in Tables 4.6-4.9.

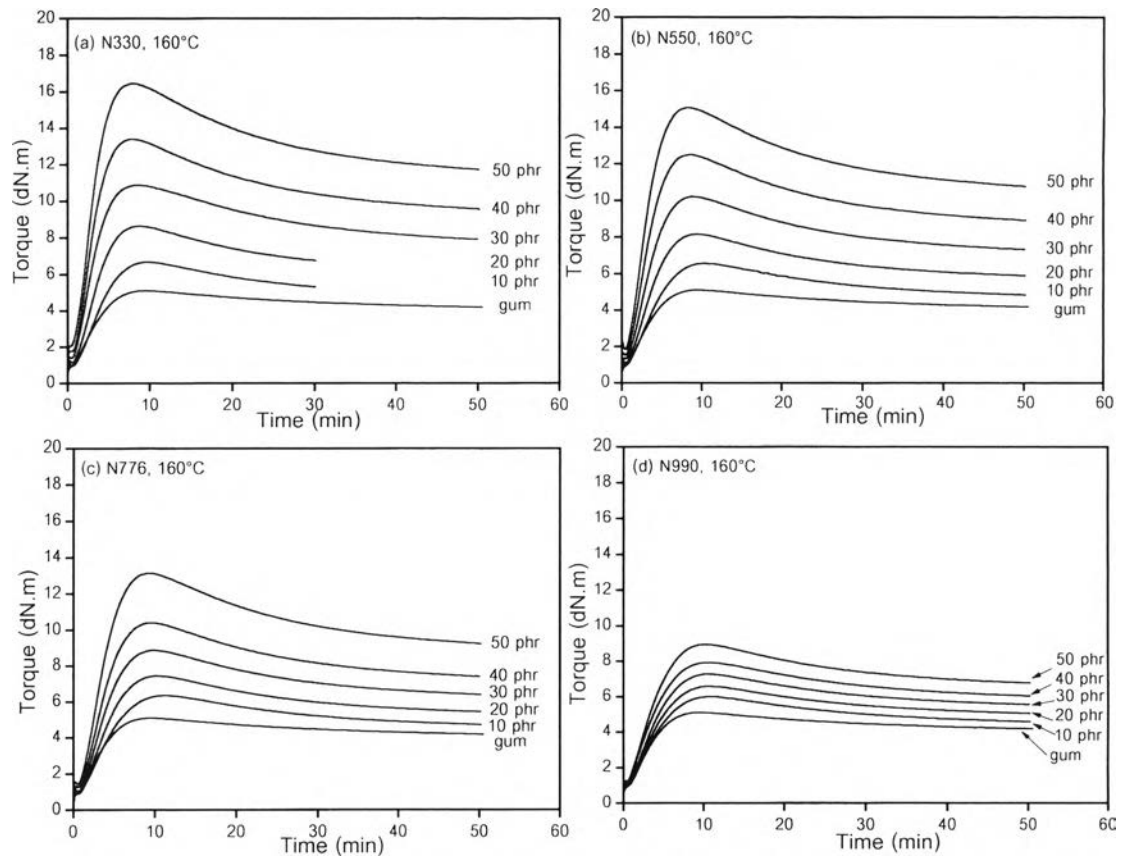


Figure 4.12 Cure curves at 160°C curing temperature of (a) N330, (b) N550, (c) N776 and (d) N990 filled NR compounds with various carbon black loadings

Table 4.6 Cure characteristics at 160°C of N330 filled NR compounds with various N330 loadings

Loading	$M_L$ (dN.m)	$M_H$ (dN.m)	$M_H - M_L$ (dN.m)	$ts_2$ (min)	$tc_{90}$ (min)	$tc_{100}$ (min)	CRI
gum	0.94	5.11	4.17	2.56	6.07	9.30	28.5
10 phr	0.95	6.68	5.73	2.50	6.40	9.52	25.6
20 phr	1.13	8.64	7.51	2.12	5.52	8.49	29.4
30 phr	1.37	10.9	9.53	1.43	5.22	8.08	26.4
40 phr	1.74	13.1	11.4	1.38	5.09	7.42	27.0
50 phr	2.02	16.5	14.5	1.26	5.09	8.06	26.1

**Table 4.7** Cure characteristics at 160°C of N550 filled NR compounds with various N550 loadings

Loading	$M_L$ (dN.m)	$M_H$ (dN.m)	$M_H-M_L$ (dN.m)	$ts_2$ (min)	$tc_{90}$ (min)	$tc_{100}$ (min)	CRI
gum	0.94	5.11	4.17	2.56	6.07	9.30	28.5
10 phr	0.99	6.56	5.57	2.52	7.01	10.2	22.3
20 phr	1.10	8.15	7.05	2.20	6.19	9.14	25.1
30 phr	1.31	10.2	8.89	1.58	5.59	8.48	24.9
40 phr	1.48	12.5	11.0	1.39	5.39	8.35	25.0
50 phr	1.78	15.1	13.3	1.26	5.25	8.27	25.1

**Table 4.8** Cure characteristics at 160°C of N776 filled NR compounds with various N776 loadings

Loading	$M_L$ (dN.m)	$M_H$ (dN.m)	$M_H-M_L$ (dN.m)	$ts_2$ (min)	$tc_{90}$ (min)	$tc_{100}$ (min)	CRI
gum	0.94	5.11	4.17	2.56	6.07	9.30	28.5
10 phr	0.88	6.36	5.48	3.00	7.32	11.0	23.2
20 phr	0.97	7.45	6.48	2.40	7.01	10.1	21.7
30 phr	1.01	8.88	7.87	2.18	6.40	9.41	23.7
40 phr	1.25	10.4	9.15	2.05	6.24	9.30	23.9
50 phr	1.41	13.1	11.7	1.47	6.13	9.15	21.5

Table 4.9 Cure characteristics at 160°C of N990 filled NR compounds with various N990 loadings

Loading	$M_L$ (dN.m)	$M_H$ (dN.m)	$M_H-M_L$ (dN.m)	$ts_2$ (min)	$tc_{90}$ (min)	$tc_{100}$ (min)	CRI
gum	0.94	5.11	4.17	2.56	6.07	9.30	28.5
10 phr	0.99	6.00	5.01	2.57	7.11	11.2	22.0
20 phr	1.03	6.58	5.55	2.45	7.07	10.2	21.7
30 phr	1.07	7.27	6.20	2.31	7.03	10.2	21.2
40 phr	1.11	7.92	6.81	2.09	6.49	10.3	22.7
50 phr	1.24	8.96	7.72	2.04	6.47	9.54	22.6

It can be seen that when carbon black loading increased, the values of both the minimum torque ( $M_L$ ) and the maximum torque ( $M_H$ ) of the carbon black filled NR compounds increased. This indicated that incorporation of carbon black into the rubber matrix led to the higher viscosity and modulus to the rubber composites. The presence of carbon black in the rubber matrix reduced the mobility of the macromolecular and consequently increased the cure torque of the compounds. The effect was more pronounced at the higher carbon black loadings as seen in Tables 4.6-4.9. And then, when considering the type of carbon black on these two parameters, it can also be seen that the N330 had the greater effect on the increasing of the minimum torque ( $M_L$ ) and the maximum torque ( $M_H$ ) than, in decreasing order, N550, N776 and N990, respectively. The smaller carbon blacks caused the rubber compounds to exhibit higher torque than the larger size ones at equal loading due to the higher extent of the rubber attaching on the carbon black surface. This led to the higher difficulty for the rubber chains to move, thus requiring the higher torque.

The changes in the scorch time, cure time and cure rate index of the NR compounds as a function of carbon black loading are shown in Figures 4.13-4.15.

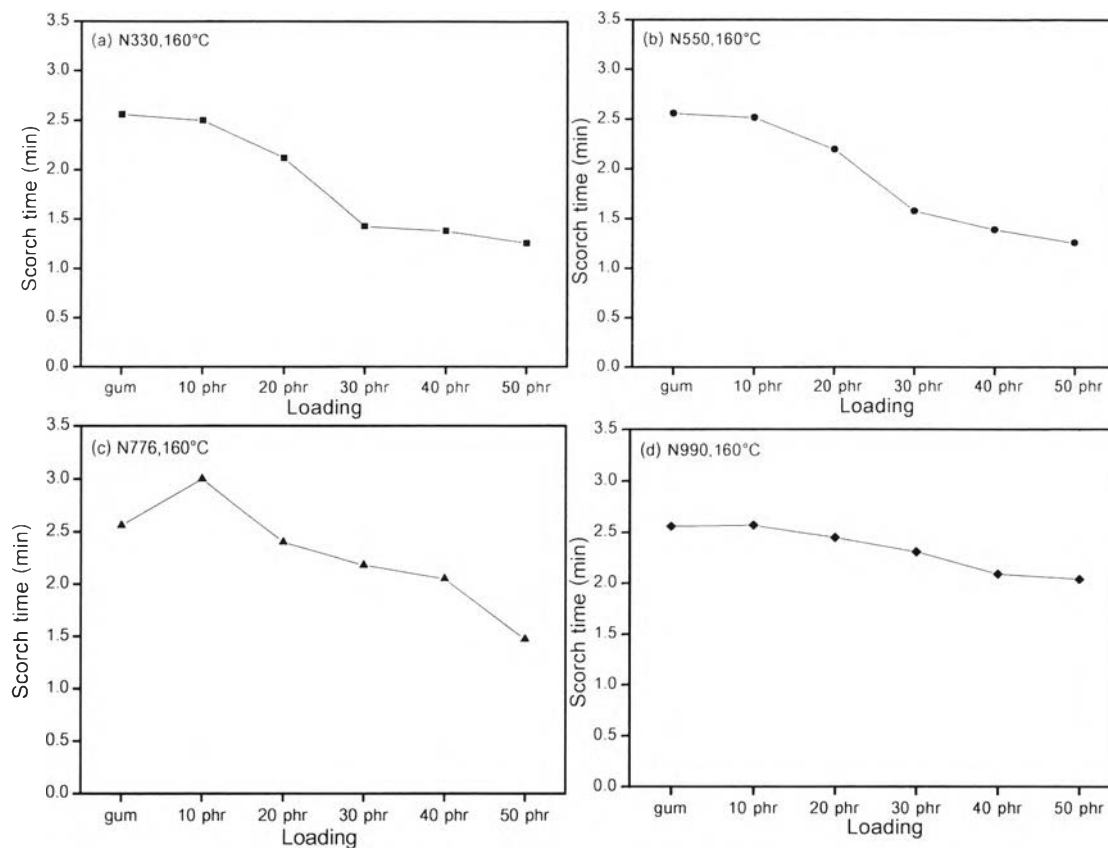


Figure 4.13 Scorch times of (a) N330, (b) N550, (c) N776 and (d) N990 filled NR compounds cured at 160°C with various carbon black loadings

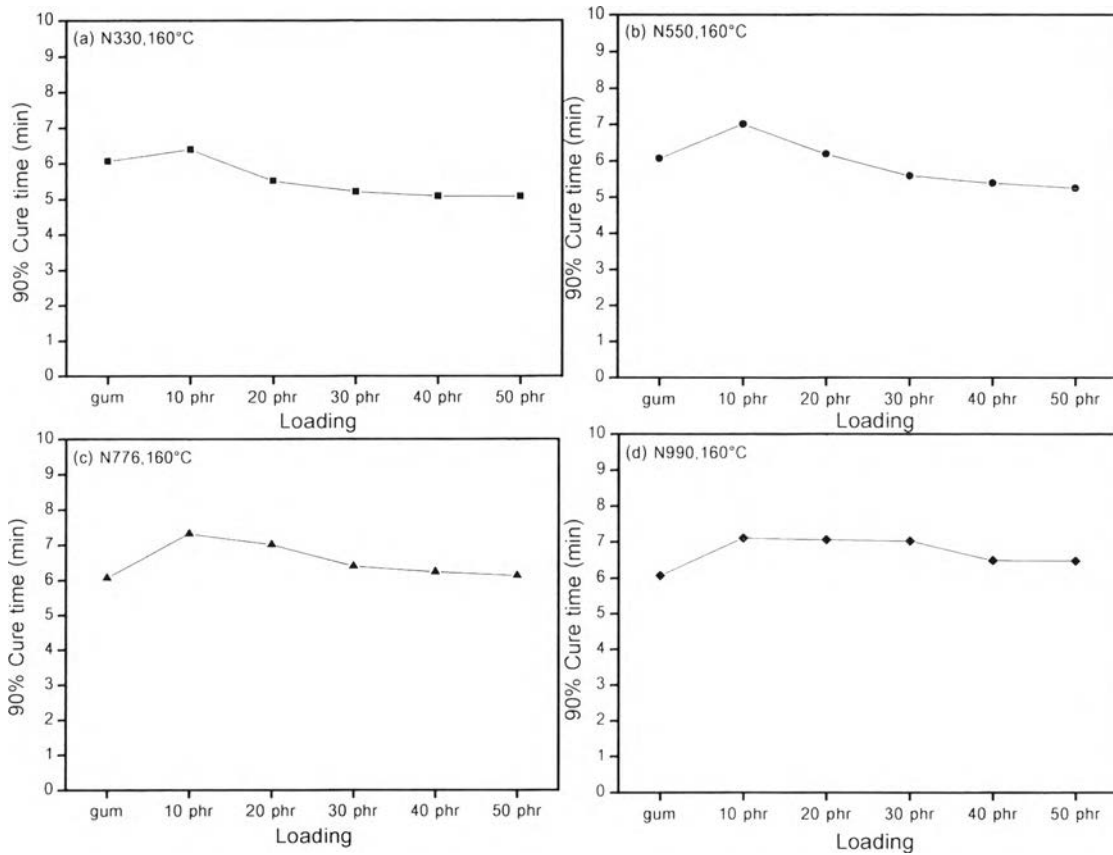


Figure 4.14 90% cure times of (a) N330, (b) N550, (c) N776 and (d) N990 filled NR

compounds cured at 160°C with various carbon black loadings

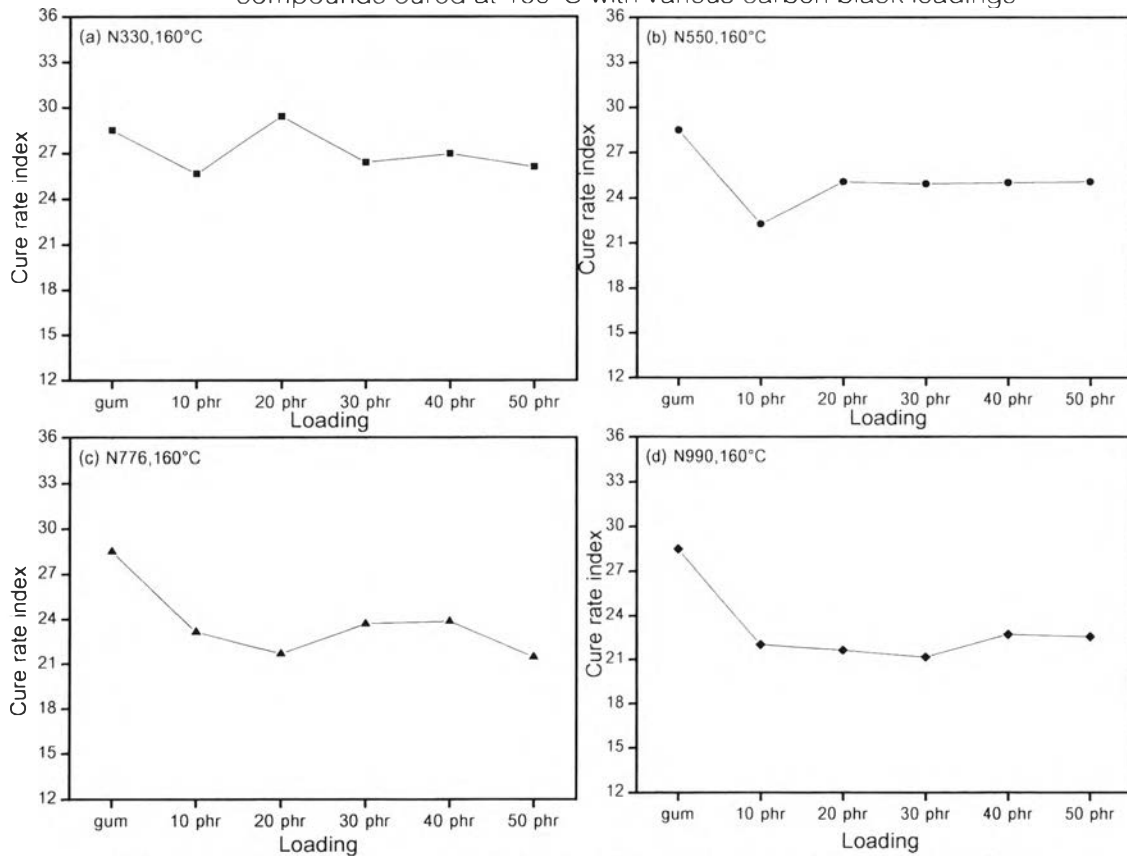


Figure 4.15 Cure rate indices of (a) N330, (b) N550, (c) N776 and (d) N990

filled NR compounds cured at 160°C with various carbon black loadings

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The results in Figure 4.13 showed that no matter which carbon black, the presence carbon black reduced the scorch time. Moreover, the reduced scorch time of the NR compounds was further decreased with increasing carbon black loadings. It was found in the previous part the change in the scorch time when 50 phr of carbon black was incorporated into the NR compounds depended on the carbon black type. The reduction of the scorch time due to incorporation of N330 was comparable to the incorporation of N550. And these two carbon blacks had greater effect on the reduction of the scorch time than N776 and N990, respectively. When considering the effect of the carbon black type on the reduction of the scorch time, there was one comment worth to point out. If the low carbon black loading for example at 10 phr was focused, the result from this study revealed that at this loading, the reduced scorch time did not depend on the carbon black type at all.

Shown in Figure 4.14 is the effect of the carbon black loading on the 90% cure times of the NR compounds for each carbon black type. Interestingly, it was found that no matter which carbon black, when the 10 phr carbon black was incorporated into the NR matrix, the 90% cure times of all carbon black filled NR compounds were higher than that of the gum one. Above 10 phr loading, the 90% cure times of the carbon black filled NR compounds now decreased with increasing carbon black loadings. In the case of N330 and N550, it was observed that the NR compounds filled with at least 20 and 30 phr of N330 and N550, respectively, would have the shorter 90% cure times than that of the gum one. For N776 and N990, although the 90% cure time also decreased with increasing loadings, the 90% cure times of the NR compounds filled with these two blacks were always higher than that of the gum one no matter which carbon black loading. Therefore, besides carbon black itself, there was the external factor that influenced on the decreasing of the cure time at high carbon black loading. Geethamma et al. [70] reported that as the filler loading increased, the incorporation time of the filler into rubber matrix also increased and consequently generated more heat due to the additional friction. The compounds with high

carbon black loading had the more severe heat history than the one with low carbon black loading. At this circumstance, some curing reaction may already occur and hence the cure time determined from the rheometer was shorter for the rubber with high carbon black loading.

Figure 4.15 showed the cure rate index at 160°C of the NR compounds with respect to the carbon black loading. It was observed that the cure rate index was not severely carbon black loading dependent. But rather the cure rate index depended strongly on the carbon black type. It was observed that the gum compound exhibited the highest cure rate index, whereas the N330 filled compound provided the highest cure rate index among other carbon black types filled NR compounds.

#### 4.2.1.4 Effect of surface activity of carbon black on cure characteristics of NR compounds

The objective of this investigation was to determine the relative contribution of carbon black surface activity to the cure characteristics. In this part, due to its high surface activity, N330 was used here. In order to judge the effect of surface activity of carbon black, all functional groups at the carbon black surface were removed by treating carbon black at high temperature (1700°C) under nitrogen atmosphere. This process is called as graphitization. Then, the study was carried out by comparing the cure characteristics of the NR compound filled with normal N330 to those of the one filled with graphitized N330 (gN330).

The cure curves showing the time dependence behavior of torque of the NR compounds filled with gN330 at loading in the range of 10 to 50 phr are depicted in Figure 4.16. The cure reaction was carried out at 160°C.

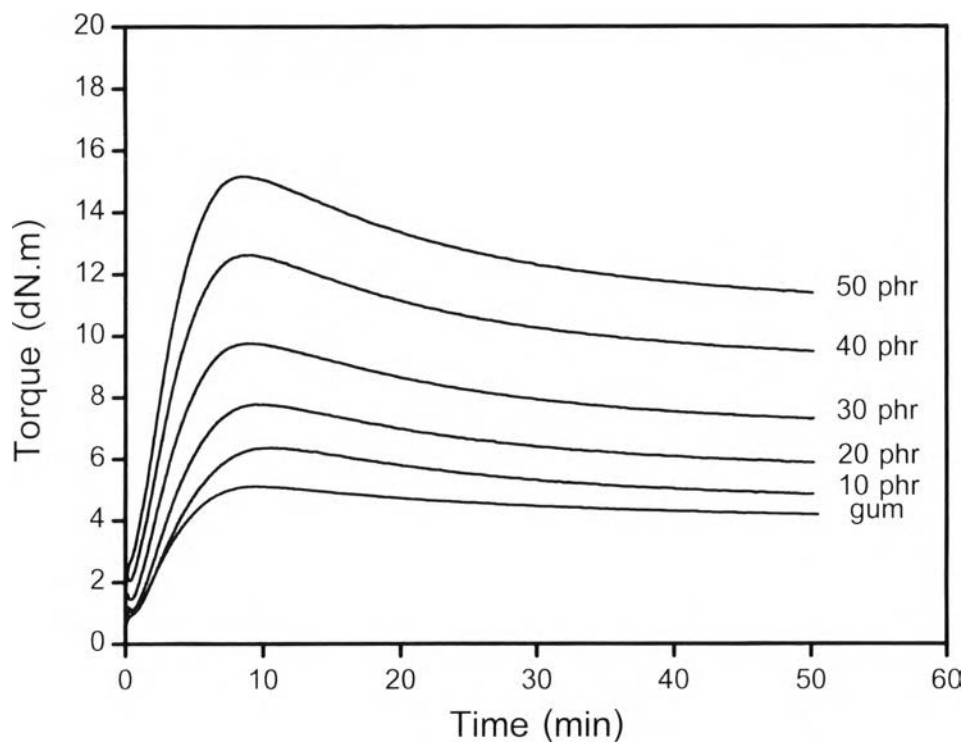


Figure 4.16 Cure curves at 160°C of gN330 filled NR compounds with various gN330 loadings

From Figure 4.16, it was clearly observed that the cure characteristics of gN330 filled NR compound depended significantly on the loading. All important cure characteristics including minimum torque ( $M_i$ ), maximum torque ( $M_H$ ), scorch time ( $t_{s_2}$ ), 90% of cure time ( $t_{c_{90}}$ ), 100% of cure time ( $t_{c_{100}}$ ) and cure rate index (CRI) of NR compound cured at different curing temperatures are deduced from Figure 4.16 and given in Tables 4.10.

**Table 4.10** Cure characteristics at 160°C of gN330 filled NR compounds with various gN330 loadings

Loading	$M_L$ (dN.m)	$M_H$ (dN.m)	$M_H-M_L$ (dN.m)	$ts_2$ (min)	$tc_{90}$ (min)	$tc_{100}$ (min)	CRI
gum	0.94	5.11	4.17	2.56	6.07	9.30	28.5
10 phr	1.02	6.37	5.35	2.52	7.01	10.3	22.3
20 phr	1.09	7.78	6.69	2.21	6.30	10.0	24.5
30 phr	1.42	9.77	8.35	1.51	5.57	8.48	24.6
40 phr	2.08	12.6	10.52	1.34	5.52	9.02	23.9
50 phr	3.05	15.2	12.15	1.31	5.53	8.32	23.7

It can be seen that when carbon black loading increased, the values of  $M_L$  and  $M_H$  of black filled NR compound increased. This was because the higher loading caused the more rubber matrix to immobilize and consequently the torque of the vulcanizates was increased [71].

The scorch times ( $ts_2$ ) at 160°C of gum, N330 and gN330 as a function of filler loading are compared in Figure 4.17. At all loadings but 40 phr, it can be seen that the NR compounds filled with gN330 displayed slightly longer scorch times than the ones filled N330. Both N330 and gN330 showed the comparable effect on the reduction of the scorch time. Therefore, the reduction of the scorch time due to the carbon black presence may not rely on the surface activity.

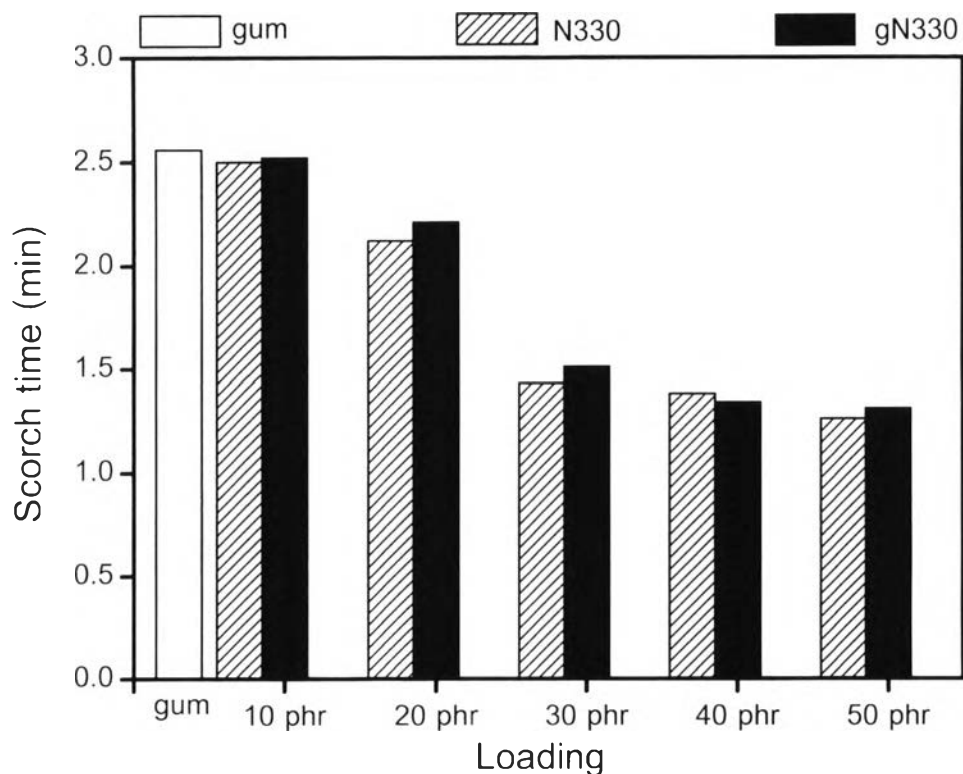


Figure 4.17 Scorch times at 160°C of gum, N330 and gN330 filled NR compounds at various filler loadings

Figure 4.18 shows the 90% cure times ( $t_{c_{90}}$ ) at 160°C of gum, N330 and gN330 filled NR compounds as a function of filler loading. It was clearly seen that the removal of functional groups at the carbon black surface reduced the ability to decrease the cure time of N330. Moreover, it was found that at loading of 10 and 20 phr, the NR filled with gN330 had the longer 90% cure time than the gum NR.

Figure 4.19 shows the cure rate indices at 160°C of gum, N330 and gN330 filled NR compounds at various filler loading. It was observed, no matter which filler loading, the NR compounds filled with gN330 exhibited the lower cure rate index than the NR compounds filled with N330.

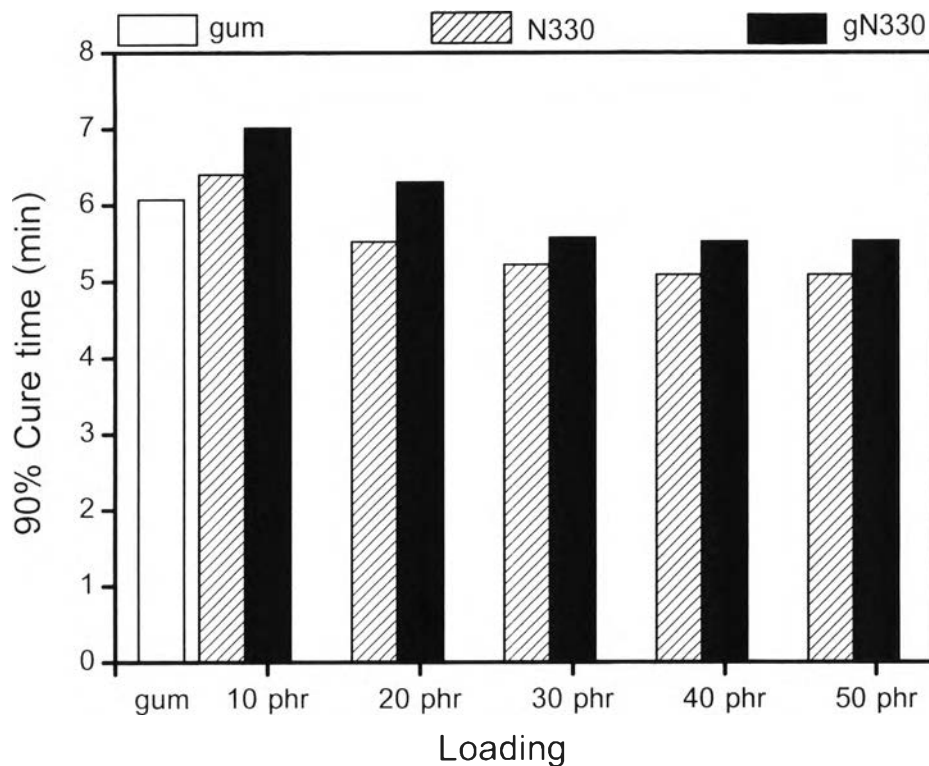


Figure 4.18 90% cure times at 160°C of gum, N330 and gN330 filled NR compounds at various filler loadings

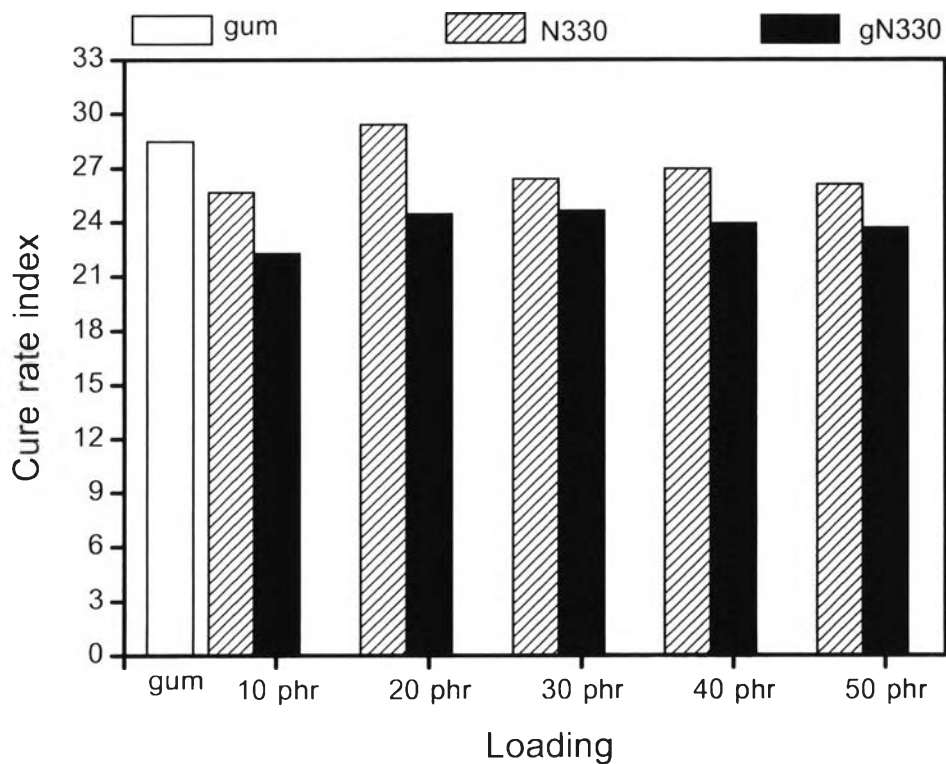


Figure 4.19 Cure rate indices at 160°C of gum, N330 and gN330 filled NR compounds at various filler loadings

## 4.2.2 Reversion Behavior of Black-Filled NR Compound

### 4.2.2.1 Effects of carbon black type on reversion behavior of NR compounds

For this part, the effects of carbon black type on the reversion behavior of NR compounds were divided into two parts. The first part was focused on the effect of the carbon black type on the initial reversion temperature. Then the second one was about the effect of the carbon black type on the reversion behavior including the plateau region and reversion rate. The discussion was conducted only on the NR filled with 50 phr carbon black.

It was found in the previous part that the reversion behavior of gum NR compound was initially observed at the curing temperature of 140°C. How the presence of carbon black at the lowest loading affected on the initial reversion temperature and the change due to the presence of carbon black was related to the carbon black type or not were first discussed. The cure curves at the different curing temperatures of NR compounds filled with various carbon blacks at 10 phr are shown in Figure 4.20.

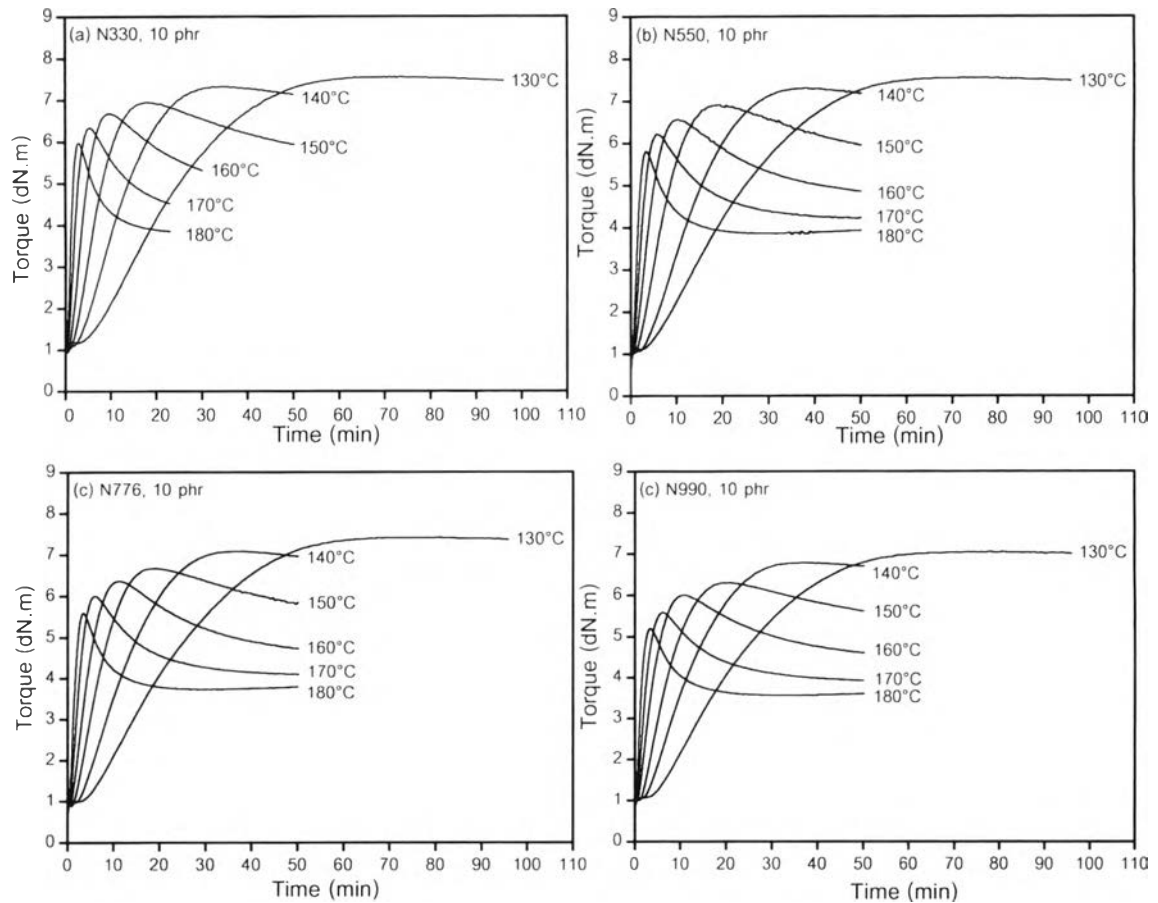


Figure 4.20 Cure curves at different curing temperatures of

(a) N330, (b) N550, (c) N776 and (d) N990 NR compounds at loading of 10 phr

It can be seen that for all 10 phr black filled NR compounds except one with N990 the reversion was initially observed at 130°C. Compared to the initial reversion temperature of the gum NR compound, the presence of carbon black caused reversion to form at the lower temperature. The result here indicated that the presence of carbon black even only 10 phr could reduce the activation energy for the reversion process. For the NR compound filled with 10 phr N990, the reversion was initially observed at the same curing temperature which was 140°C as the gum NR compound. The study on the effect of N990 on the initial reversion temperature was further investigated. Shown in Figure 4.21 was the cure curves at 130°C of N990 filled NR compounds with loading 10 to 50 phr. The result showed that to cause the reversion at 130°C, the NR compound must be loaded with N990 at least 20 phr.



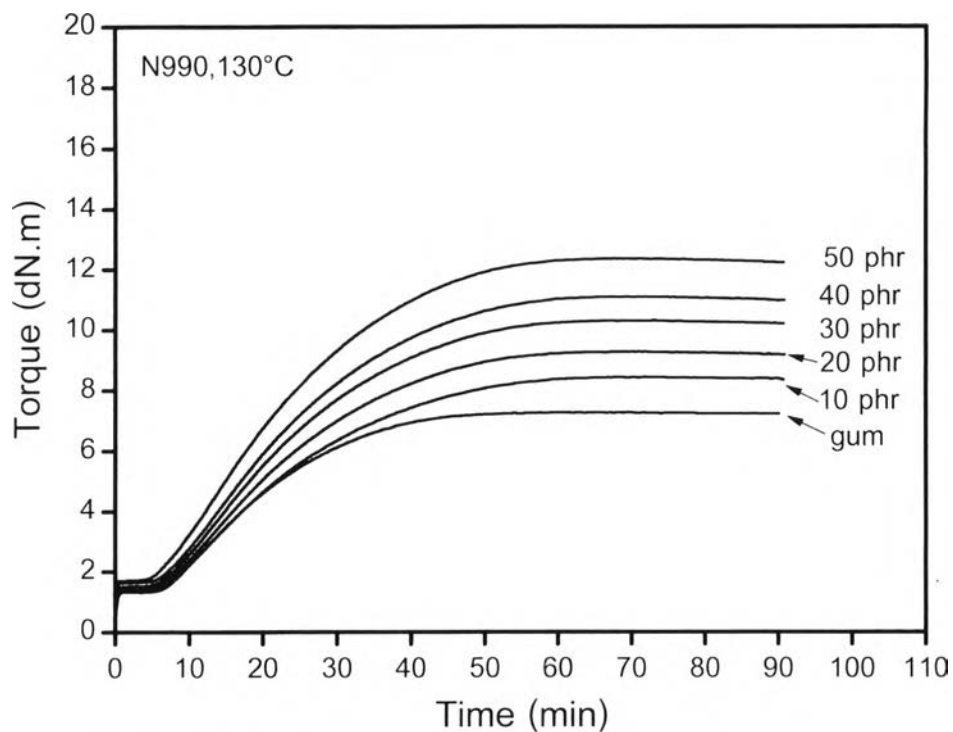


Figure 4.21 Cure curves at 130°C of N990 filled NR compounds  
at various N990 loadings

Now, the effect of carbon black type on the reversion behavior including plateau region and reversion rate was focused. The results used to discuss in this part were taken from the cure curves at different curing temperatures of the NR compounds filled with various carbon blacks at 50 phr loading. Comparison of the plateau region and the reversion rate between gum and carbon black filled NR compounds are shown in Figures 4.22-4.23.

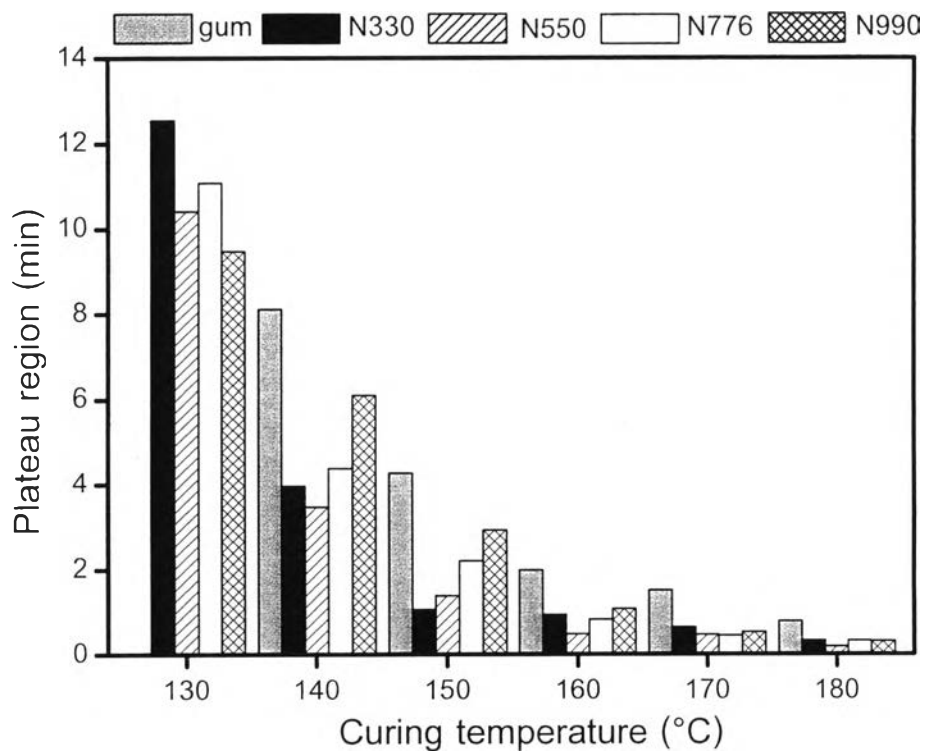


Figure 4.22 Plateau regions of gum and black filled NR compounds at different curing temperatures

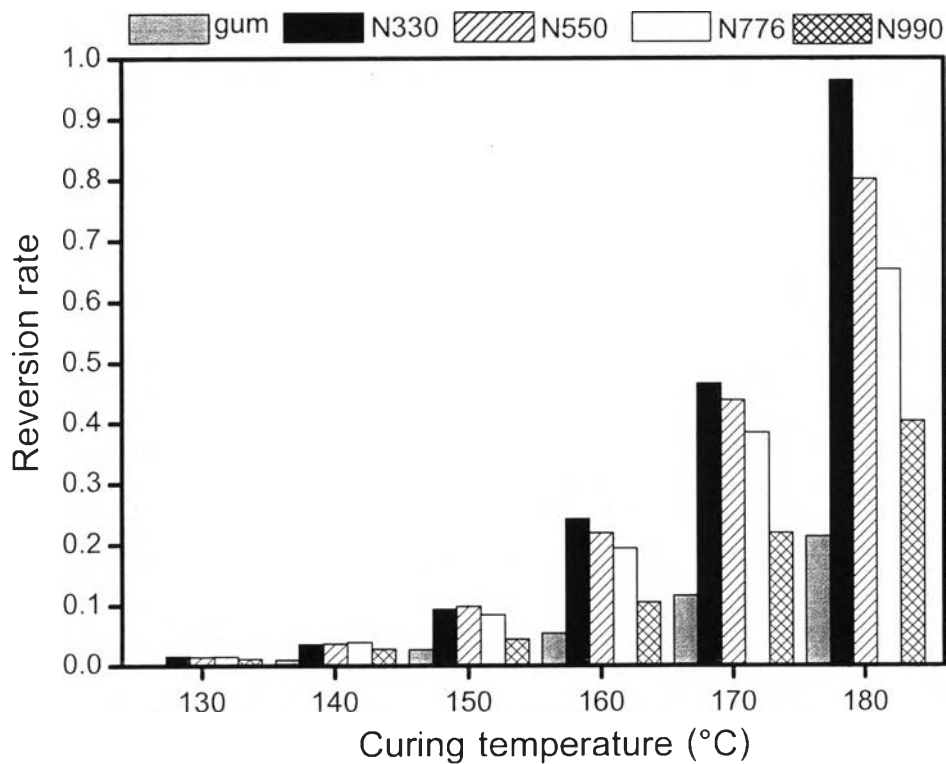


Figure 4.23 Reversion rate of gum and black filled NR compounds at different curing temperatures

The result in Figure 4.22 showed that at all curing temperatures the incorporation 50 phr carbon black into the rubber caused the lower reversion resistance network. This was indicated by the noticeably shorter plateau region compared to that of the gum one. The shortening of the plateau region depended strongly on the carbon black type. At all curing temperatures except 160°C, the N550 carbon black had greater ability to shorten the plateau region than, in the decreasing order, N330, N776 and N990. For that excluding temperature, the NR compound filled with N330 had shorter plateau region than the one filled with N550.

The result shown in Figure 4.23 revealed that the incorporation of all carbon blacks into the NR compounds, no matter which curing temperature, gave the faster reversion rate to the carbon black filled NR compounds than the gum one. The evaluation of the effect of the carbon black type on the reversion rate showed that N330 and N550 seemed to have the highest comparable effect on the fastening reversion rate. And N776 showed the less effect, whilst N990 showed the least effect on the fastening reversion rate. Interestingly, when looking back at the effect of the carbon black type on the cure time, it was found that the carbon black which had greatest effect on the shortening the cure time also caused the fastest reversion rate to the NR compound. Kok [72] examined the effect of several compounding ingredients on the reversion of accelerated sulfur vulcanization of natural rubber (NR). The result revealed that accelerators which normally provide fast cures are found to cause more severe reversion than slower accelerators. The explanation given for this is because the faster cures reduce the desulfuration reaction, thus resulting the networks in having the higher polysulfidic linkages. The higher sulfur ranks in the network has the lower thermal stability and hence the higher extent of reversion is observed. Similar to the fast accelerator, the result in this study showed the presence of certain carbon black accelerated the curing reaction. Therefore, it was proposed here the higher reversion rate observed in the particular black filled NR compound might be due to the lower desulfuration during the curing reaction.

#### 4.2.2.2 Effect of carbon black loading on reversion behavior at 160°C of NR compounds

The effect of carbon black loading on the reversion behavior of the NR compounds cured at 160°C was discussed in this part. Figure 4.24 showed the effect of carbon black loading on the plateau region and the reversion rate of each black filled NR compound. At the curing temperature of 160°C, it can be seen that the presence of 10 phr carbon black no matter which type initially increased the plateau region compared to the gum one. However, as the loading of carbon black was increased then, it resulted in a continuous decrease in the plateau region with comparable value to that of the gum NR compound at the carbon black loading of 40(N330), 20(N550), 30(N776) and 40(N990) phr. Therefore, at the highest carbon black loading, 50 phr, all black filled NR compounds had the shorter plateau region to the gum one. When considering the effect of carbon black loading on the reversion rate as shown in Figure 4.24, it can be clearly seen that the increase in the carbon black loading caused the higher reversion rate. This was because the desulfuration process was also influenced by the amount of carbon black. This can be supported by the reduction of the cure time with increasing the carbon black loading as shown in Figure 4.12. Therefore, this should lead to the higher polysulfidic crosslink. Therefore, the reversion rate should also increase at high carbon black loading due to the higher polysulfidic crosslinks to decompose at the prolonged cure time.

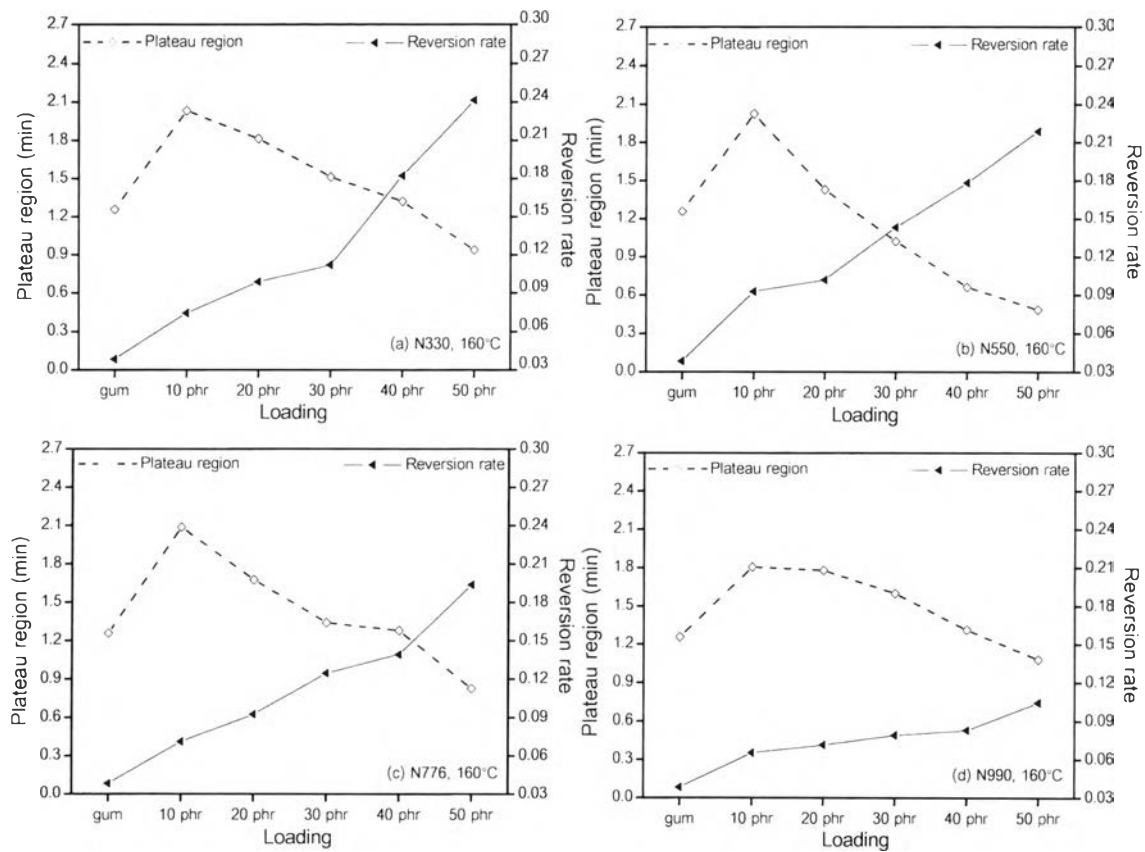


Figure 4.24 Plateau regions and reversion rates at 160°C of (a) N330, (b) N550, (c) N776 and (d) N990 filled NR compounds with various carbon black loadings

#### 4.2.2.3 Effect of surface activity of carbon black on reversion behavior at 160°C of NR compounds

The reversion behavior at 160°C of the NR filled with N330 was compared to that of the one filled with gN330 as shown in Figures 4.25-4.26.

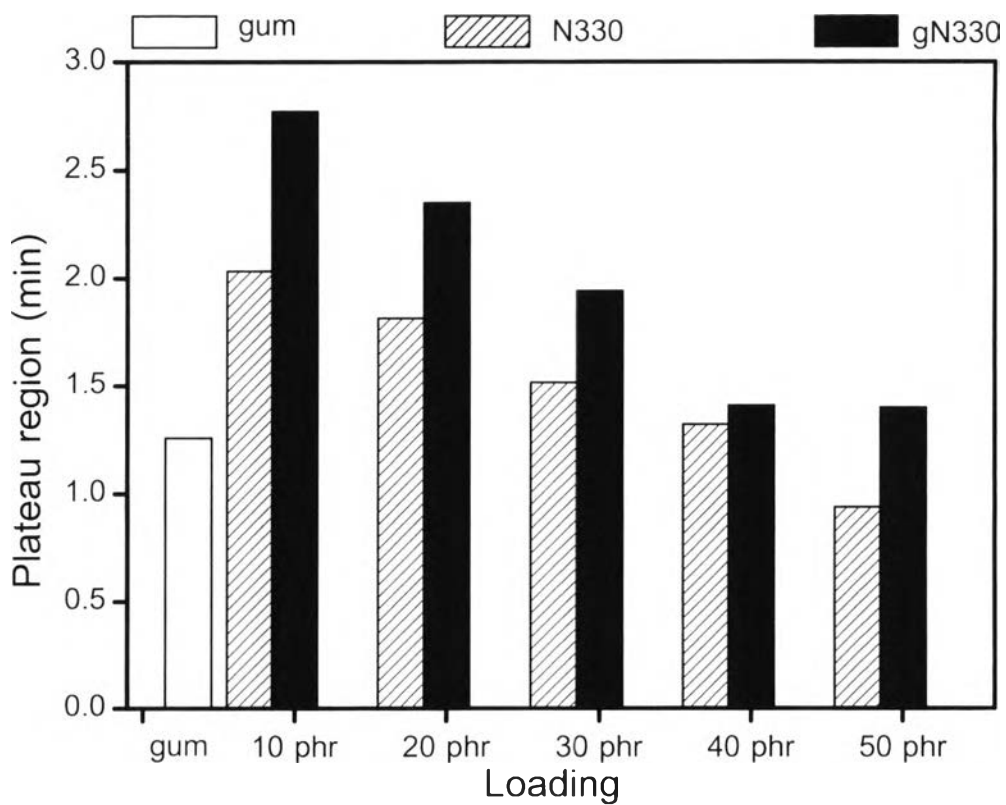


Figure 4.25 Plateau regions at 160°C of gum, N330 and gN330 filled NR compounds

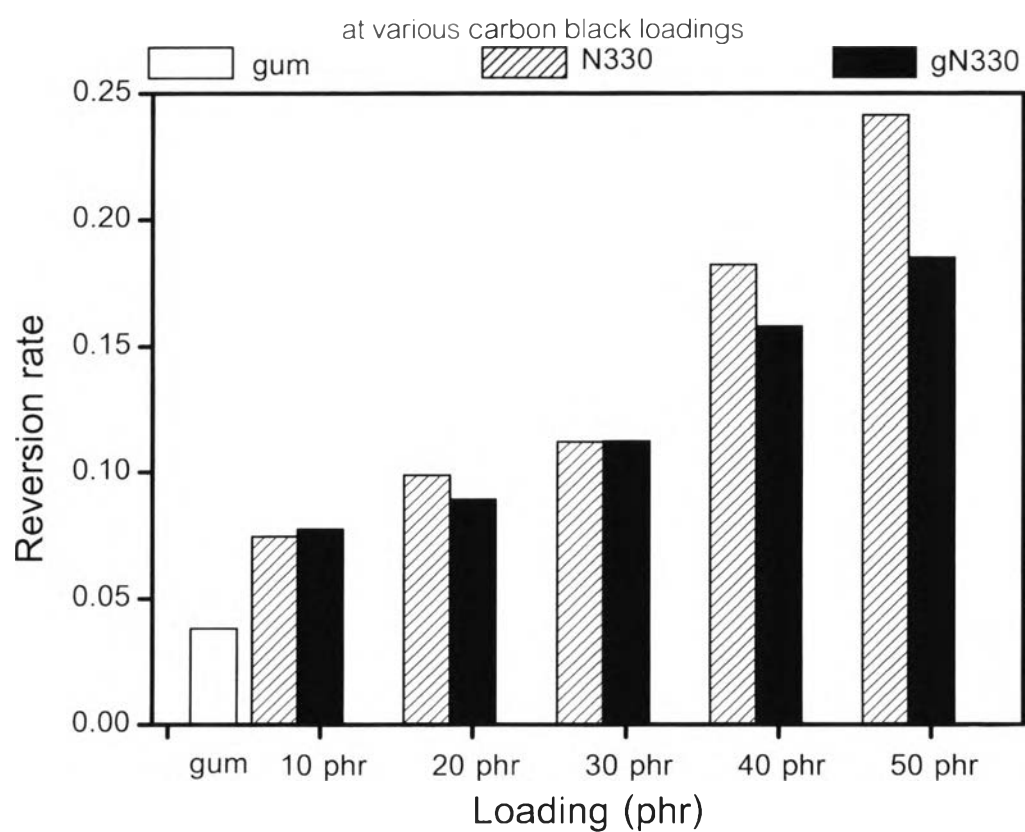


Figure 4.26 Reversion rates at 160°C of gum, N330 and gN330 filled NR compounds

at various carbon black loadings

At the curing temperature of 160°C, for both N330 and gN330, increasing carbon black loading shortened the plateau region. When considering the effect of surface activity, it can be seen that no matter which carbon black loading, the NR compounds filled with gN330 always had longer plateau regions than the ones filled with N330. Result in Figure 4.26 showed that for both N330 and gN330, increasing carbon black loading caused the faster reversion rate. Comparison between N330 and gN330 at the same loading, it was found that replacing N330 with gN330 gave NR compound a slower reversion rate. Therefore, the removal of any functional group at carbon black surface seemed to have superior effect on reversion resistance. The reason why the surface activity of carbon black had so much effect on the reversion behavior could be explained based on its effect on the cure characteristics. From Figures 4.17-4.19, it was shown that after removing all functional groups on the N330 surface, this carbon black had lower ability to accelerate the curing reaction. Therefore, the NR compound filled with gN330 had more chance to undergo desulfuration process. The obtained network was made from the lower sulfur ranks which had the higher thermal stability. And this might be the most possible reason for higher reversion resistance when N330 was substituted by gN330.

#### 4.2.3 Thermal Aging Properties of Carbon Black Filled NR Compounds

The effect of carbon black type and loading on the thermal aging properties of NR compounds cured at 160°C with the 90% cure time ( $t_{c_{90}}$ ) was discussed in this part.

##### 4.2.3.1 Effect of carbon black type on thermal aging properties of NR compounds

The 100% modulus (M100), % elongation at break (EB) and tensile strength (TS) before and after thermal aging and their relative values of 50 phr N330, N550, N776, N990 and gN330 filled NR compounds cured at 160°C with 90% cure time is shown in Figures 4.27-4.29.

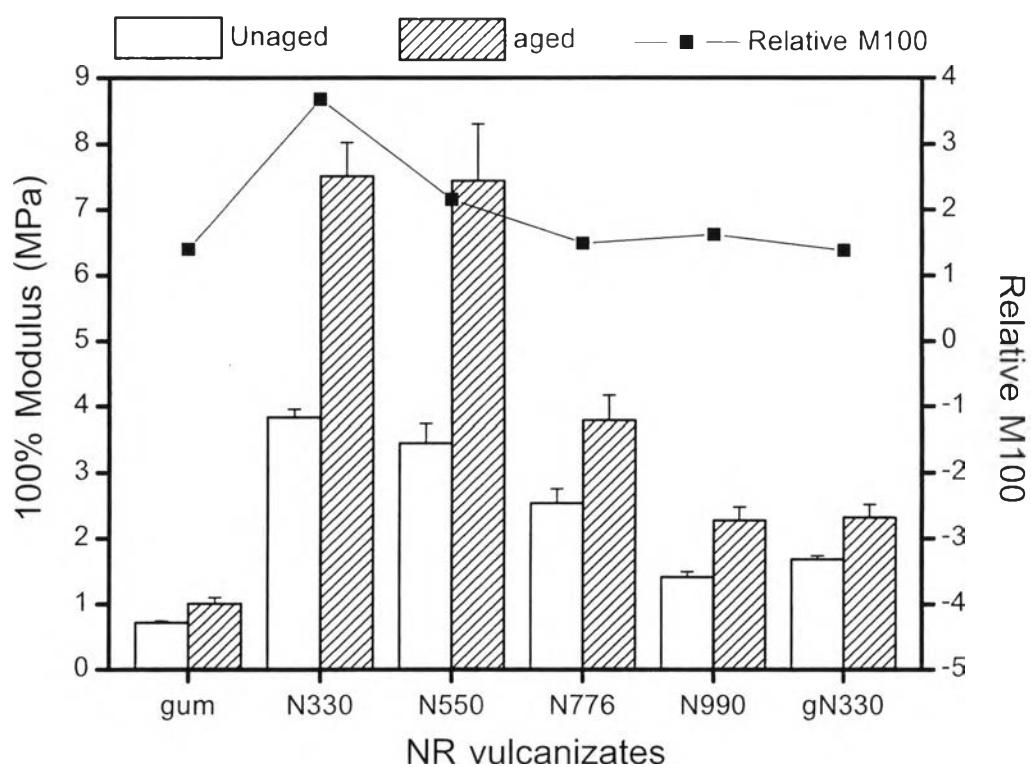


Figure 4.27 100% modulus before and after thermal aging and their relative values of 50 phr N330, N550, N776, N990 and gN330 filled NR compounds



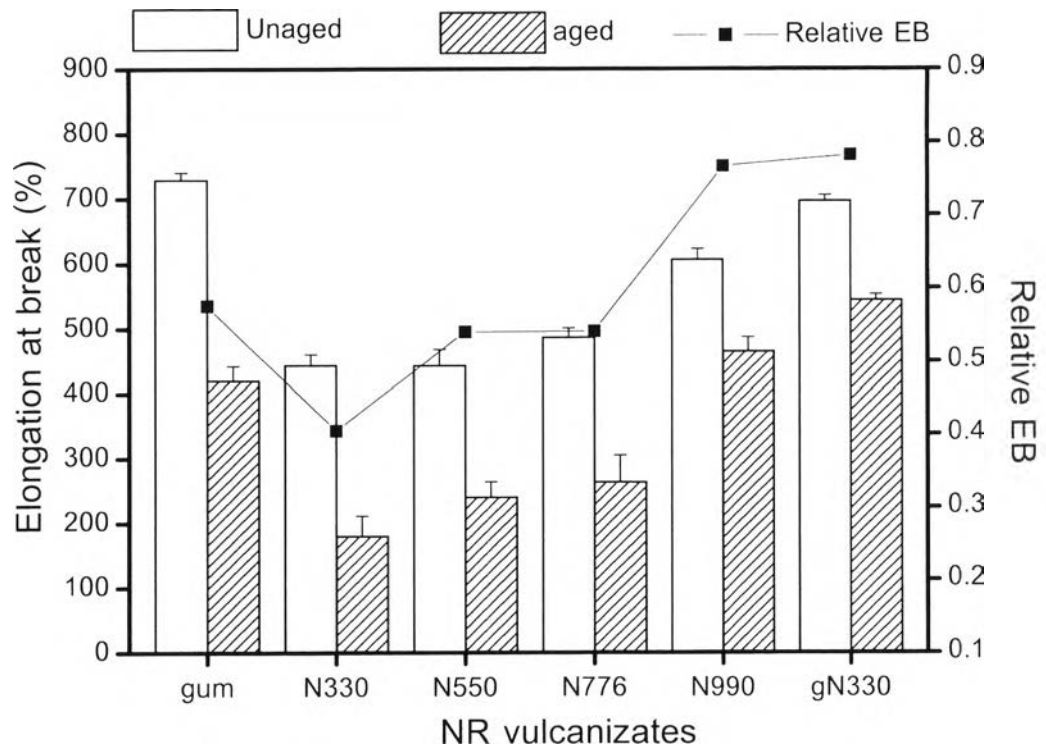


Figure 4.28 Elongation at break (%) before and after thermal aging and their relative values of 50 phr N330, N550, N776, N990 and gN330 filled NR compounds

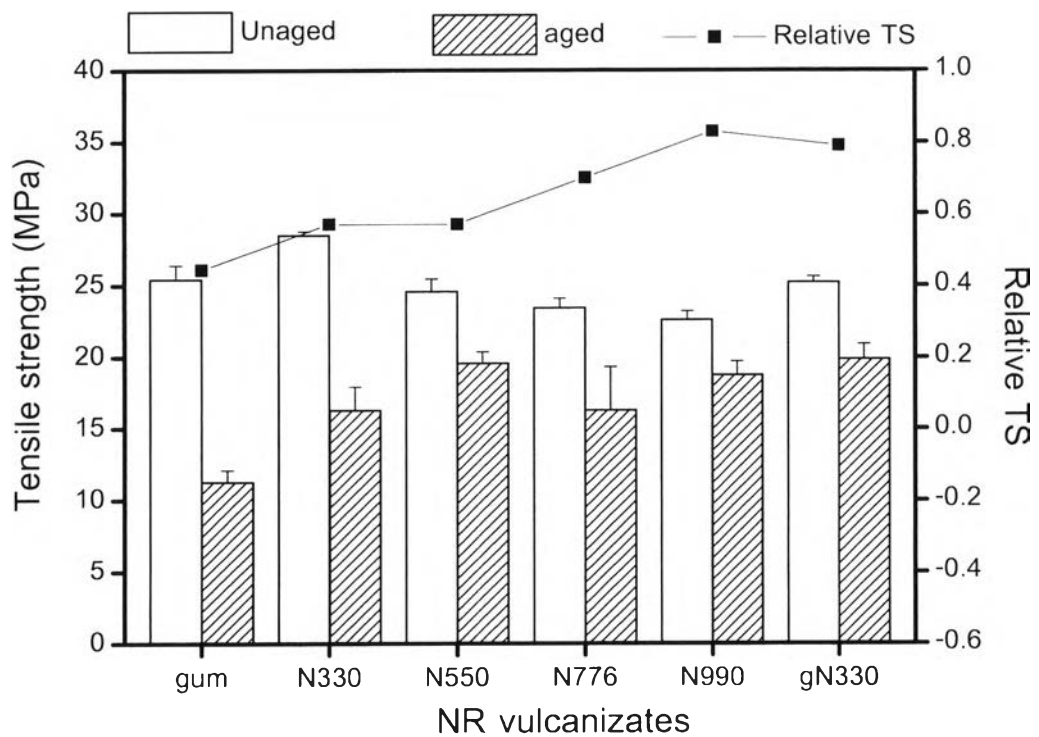


Figure 4.29 Tensile strengths before and after thermal aging and their relative values of 50 phr N330, N550, N776, N990 and gN330 filled NR compounds

As shown in Figure 4.27, before aging the incorporation of carbon black into the rubber matrix resulted in higher 100% modulus no matter which carbon black type when compared to that of the gum compound. Besides, the hydrodynamic effect, the significant increase in 100% modulus was also due to the strain amplification effect [73]. As the rigid filler does not share in the deformation, it is clear that the inclusion of a rigid adhering filler in a soft matrix will cause the average local strain in the matrix to exceed the macroscopic strain. Thus the rubber in the filled vulcanizate finds itself more highly strained and responds with a higher stress as shown in Figure 4.28. In Figure 4.28, it was observed that the strain amplification depended strongly on the carbon black type. At the same carbon black loading, the NR compound filled with N330, smallest carbon black, had the highest 100% modulus. The small particle black provided much more surface area for rubber chains to adhere on. Clearly, the increase in 100% modulus was varied proportionally to the surface area. However, when comparing between N330 and gN330, it was found the removal of functional groups at the N330 surface resulted in the significant decreased in 100% modulus. Therefore, to form bonding between the rubber chain and carbon black surface, only large surface area was not enough. The carbon black surface must provide enough functional groups. After extensively exposing to high temperature under air, all rubber compounds both with or without carbon black had higher 100% modulus. The increased modulus indicated that the aged specimens had higher crosslink density. This was confirmed by the increase in crosslink densities determined the swelling method in Figure 4.30. When considering the effect of carbon black type on the increase in the 100% modulus after thermal aging, the highest relative M100 was observed for both N330 and N550 filled compounds. The N776 and N990 and gN330 filled NR compounds had comparable relative M100 which was closer to one than those of the ones filled with N330 and N550. The obtained result informed that both N330 and N550 filled NR vulcanizates had less thermal stability than the NR vulcanizates filled N776 and N990 and gN330. When comparison N330 with gN330, it was found that the removal of functional groups on the N330 surface

resulted in the higher thermal aging resistance networks. This was indicated by the less change in 100% modulus of gN330 filled NR compound after aging.

The increase in the crosslink density after aging reduced the mobility of the rubber chains. As a consequence, the aged specimens could be extended less, thus resulting in having lower %EB as shown in Figure 4.28. Thermal aging had most effect on the relative EB of the NR compound filled N330.

Shown in Figure 4.29 was the effect of carbon black type on the relative TS. Several points were worth to point out here. Let start from the effect of carbon black type on the tensile strength of the vulcanizates before thermal aging. The presented result showed that the reinforcing efficiency depended strongly on the carbon black type. It was found that amongst carbon blacks used under this study, there was only the NR vulcanizate filled with N330 that showed higher tensile strength than the gum vulcanizate. The tensile strength of the NR vulcanizates decreased proportionally with decreasing carbon black surface area as a following order: N330, N550, N776 and N990. The tensile strength of the NR vulcanizate filled gN330 was lower than the one filled with N330 but slightly higher than the ones filled with N550, N776 and N990. This confirmed that the tensile strength depended mainly on the carbon black surface area. Now let consider the tensile strength of the NR vulcanizates after thermal aging. It can be seen that tensile strength of gum and black filled NR vulcanizates tended to decrease after treatment at high temperature. This may be because the degree of crosslinking after aging exceeds an optimum value and the networks became too dense, leading to the decrease in tensile strength. The gum NR vulcanizate still showed the lowest tensile strength. Interestingly, after exposing to heat for a certain time, it was found that amongst various black filled vulcanizates, the one filled with N330 now had nearly the lowest tensile strength. The rests but N776 seemed to have comparable tensile strength. For the black filled vulcanizates, the relative TS of the N990 filled vulcanizate was slightly greater than that of the ones filled with N774, N550 and N330. This meant the vulcanizate filled with N990 had the greater thermal aging resistance. Comparison between

N330 and gN330, it can be seen that the vulcanizate filled with gN330 had higher thermal aging resistance. This can be indicated by the higher relative TS as shown in Figure 4.29. Moreover, after aging, gN330 gave vulcanizates with higher tensile strength than N330.

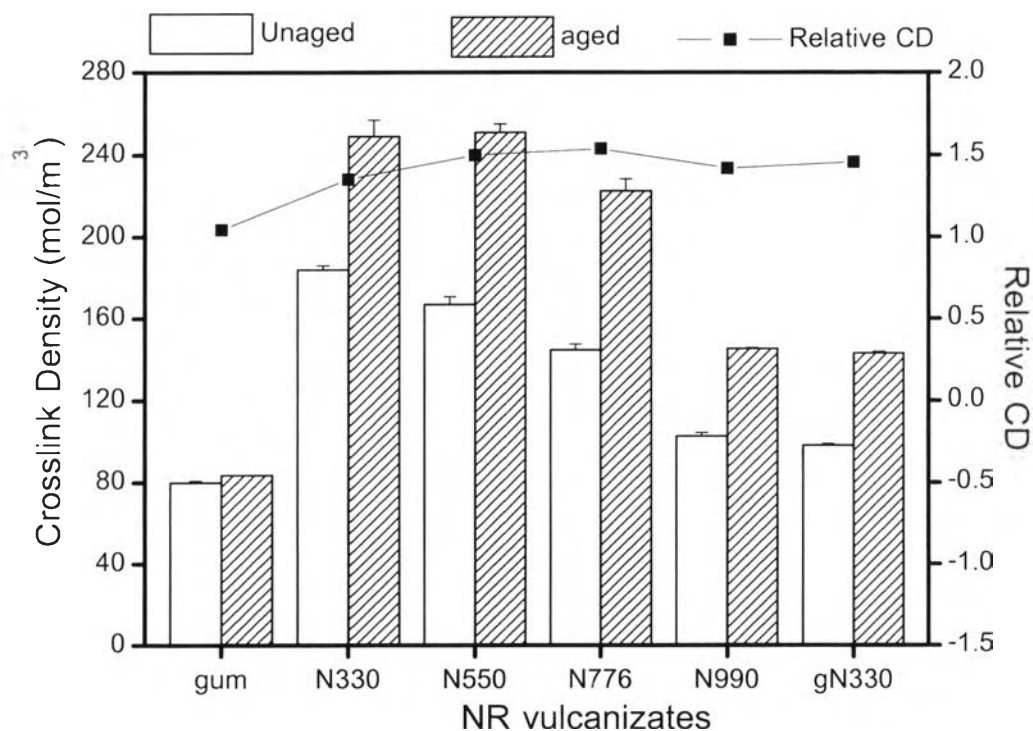


Figure 4.30 Crosslink densities (CD) before and after thermal aging and their relative values of 50 phr N330, N550, N776, N990 and gN330 filled NR compounds

#### 4.2.3.2 Effect of carbon black loading on thermal aging properties of NR compounds

The effect of carbon black loading on thermal aging properties of NR compounds for each carbon black are shown in Figures 4.31-4.35. The compounds were cured with  $t_{c_{90}}$ . When there is the change in crosslink density which is relevant to the change of 100% modulus will lead the NR vulcanizate in having different elongation at break and also tensile strength. Therefore, the discussion on effect of carbon black loading on thermal aging properties was focused only on the change in relative M100.

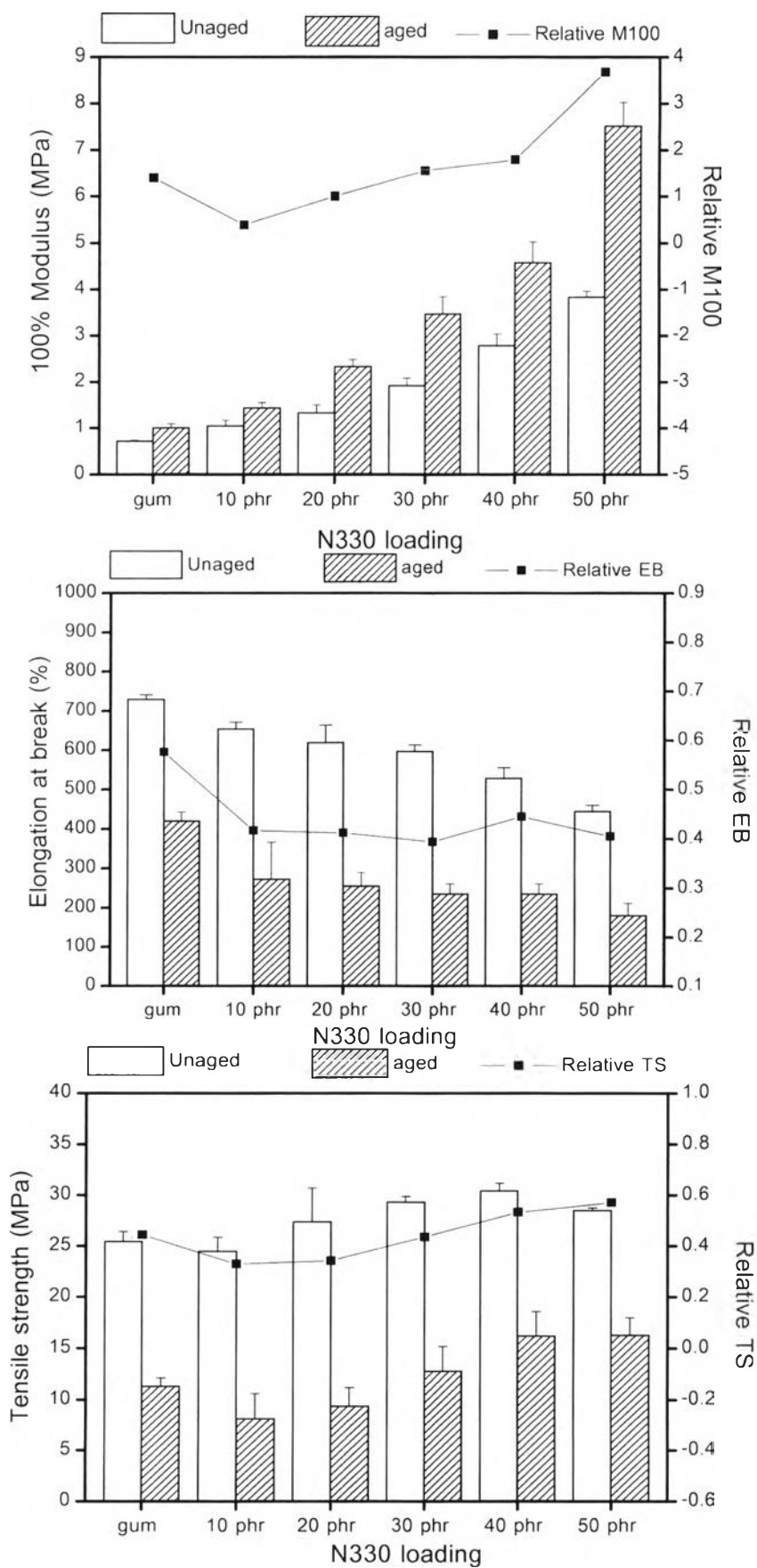


Figure 4.31 100% modulus (M100), % elongation at break (EB) and tensile strength (TS) before and after thermal aging and their relative values of N330 NR vulcanizates at  $t_{c90}$

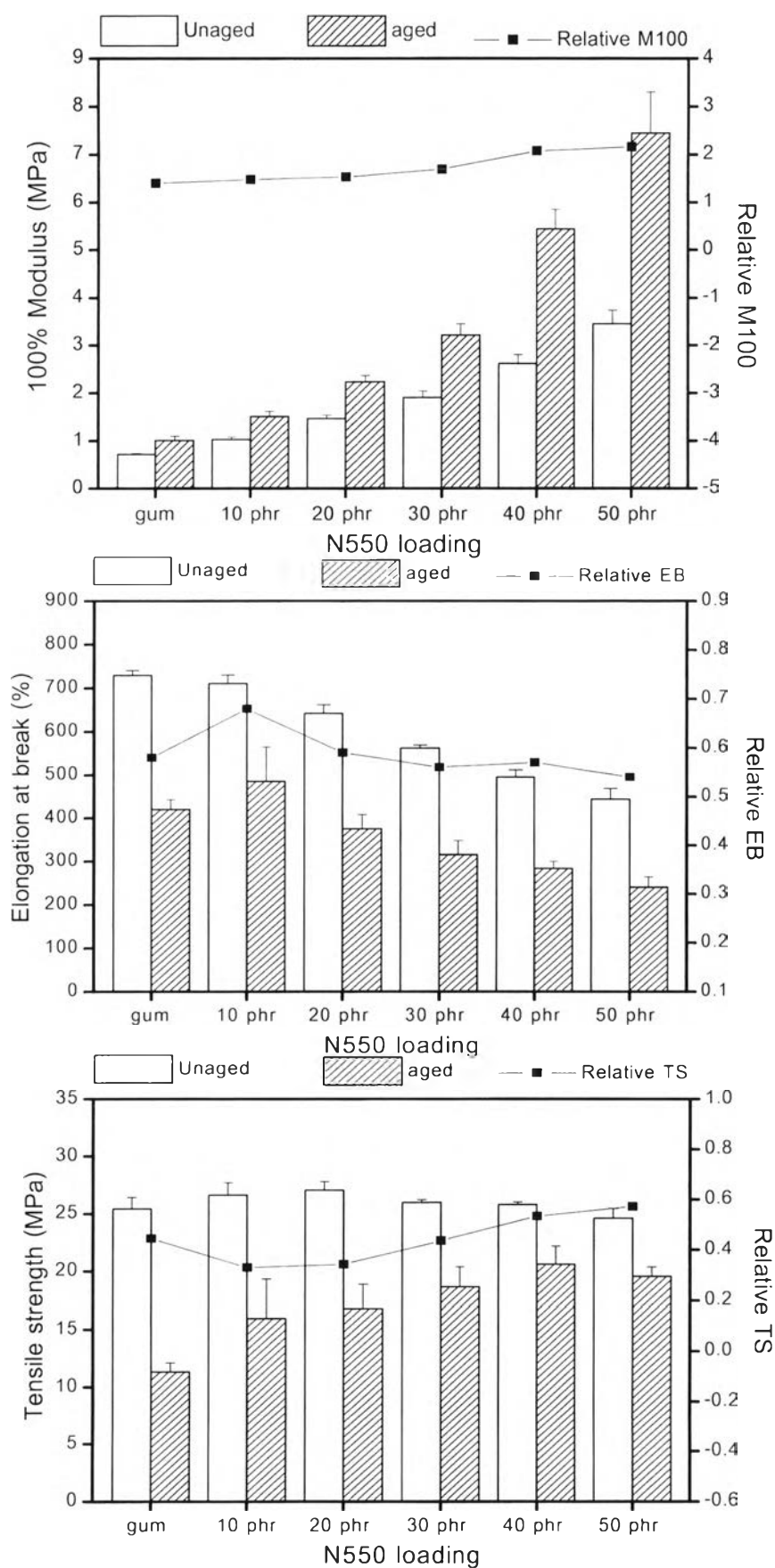


Figure 4.32 100% modulus (M100), % elongation at break (EB) and tensile strength (TS) before and after thermal aging and their relative values of N550 NR vulcanizates at  $t_{c90}$

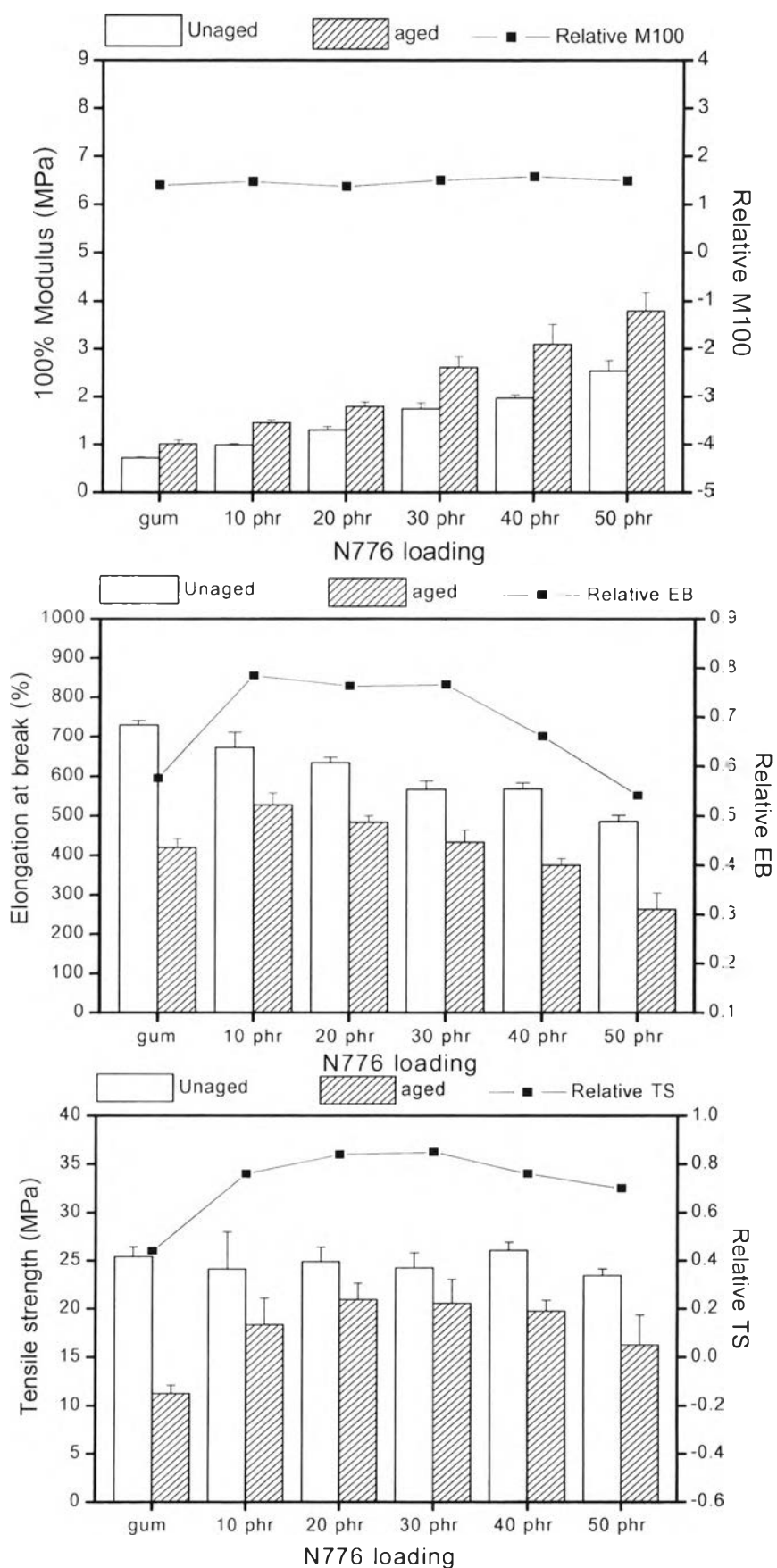


Figure 4.33 100% modulus (M100), % elongation at break (EB) and tensile strength (TS) before and after thermal aging and their relative values of N776 NR vulcanizates at  $t_{c_{90}}$

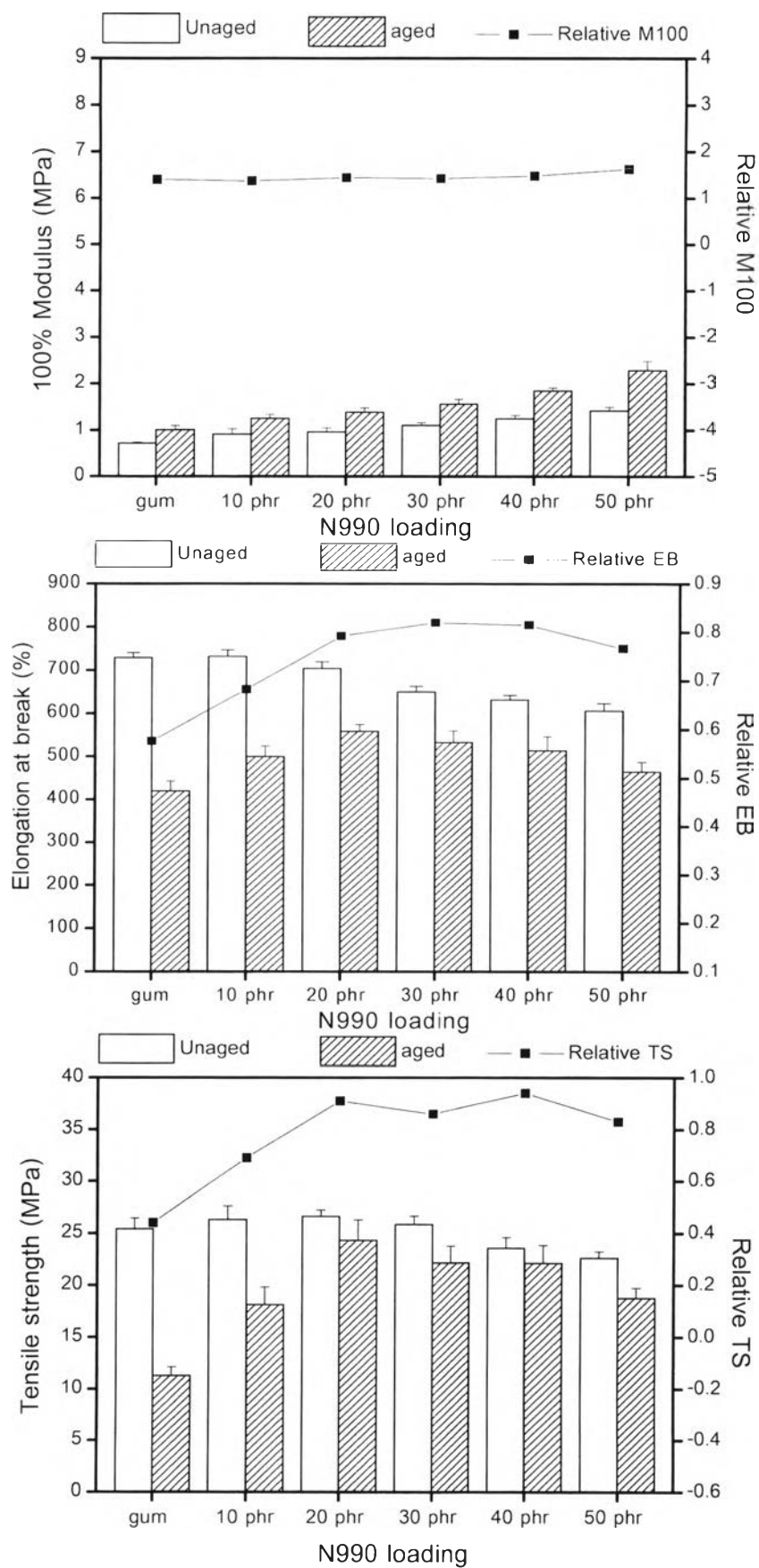


Figure 4.34 100% modulus (M100), % elongation at break (EB) and tensile strength (TS) before and after thermal aging and their relative values of N990 NR vulcanizates at  $t_{c_{90}}$



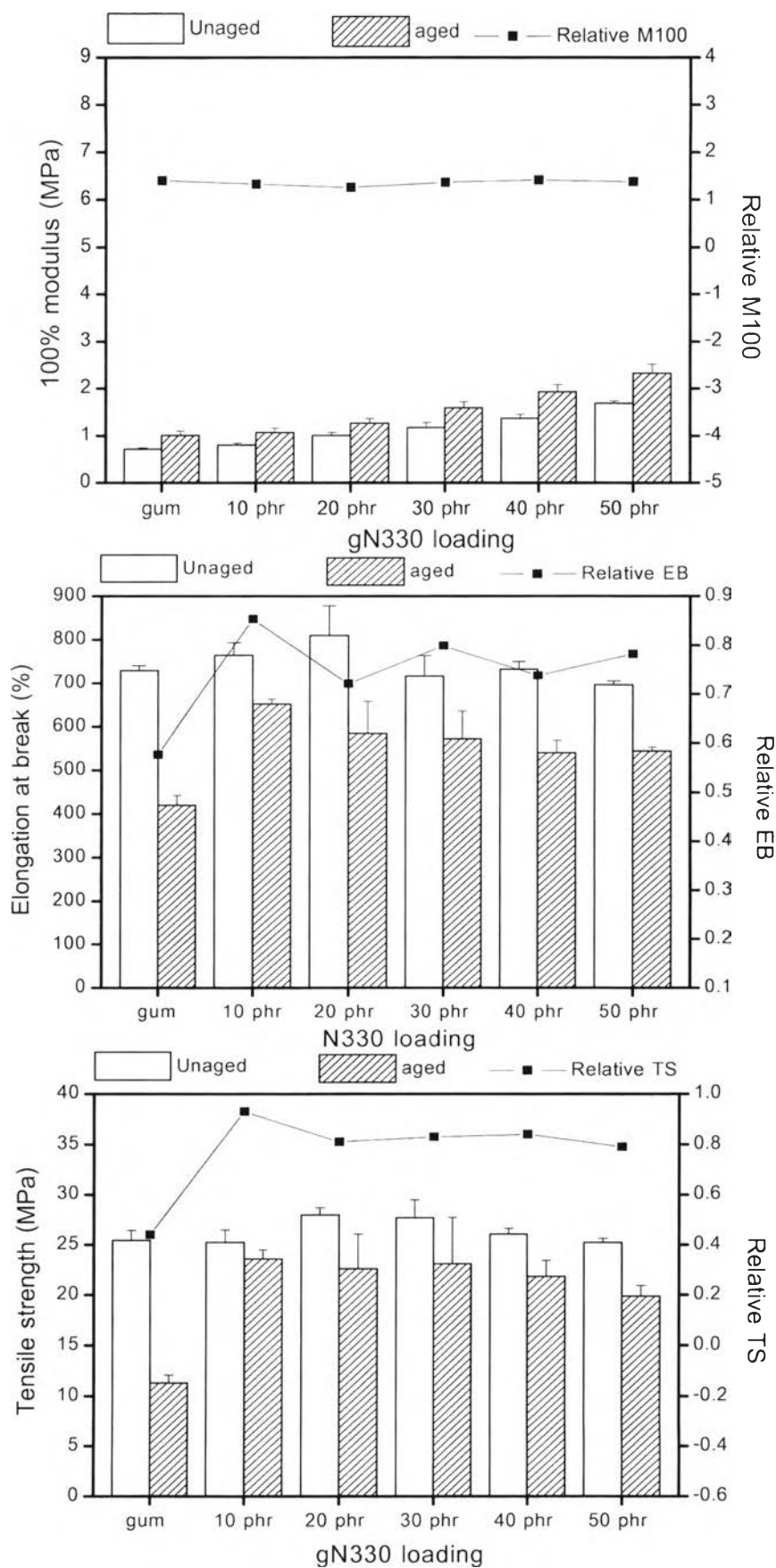


Figure 4.35 100% modulus (M100), % elongation at break (EB) and tensile strength (TS) before and after thermal aging and their relative values of gN330 NR vulcanizates at  $t_{c_{90}}$

As can be seen in Figures 4.31-4.35, the effect of carbon black loading on the relative M100 depended on carbon black type. The changes in the relative M100 with respect to the carbon black loading due to each carbon black were compared in Figure 4.36.

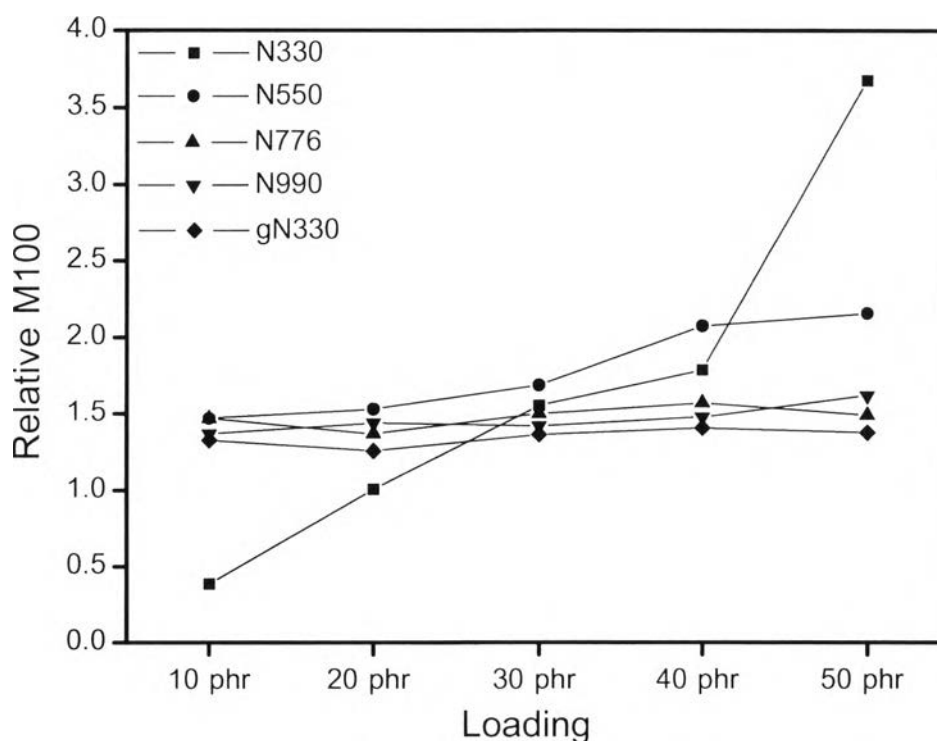


Figure 4.36 Relative 100% modulus of NR vulcanizates of N330, N550, N776, N990 and gN330 filled NR compounds with various loadings

The result presented above indicated that increasing N330 loading from 10 to 50 phr clearly increased the relative M100. This was indicated by the highest slope. When the relative M100 was further away from one meant the vulcanizate underwent more degradation. The relative M100 of the NR compounds filled N550 also increased with increasing the N550 loading. But the slope was less than that of N330. When considering the effect of N776 and N990 loading on the relative M100, it was found that the relative M100 did not depend on the loading of those two carbon blacks at all. This meant thermal degradation of the NR compounds filled with these two carbon blacks did not increase with increasing loading.

### 4.3 Sulfur Crosslink Distribution of NR Vulcanizates

The changes of overall sulfur crosslink distribution of gum and N330 and N550 filled NR vulcanizates with respect to curing time were determined using X-ray absorption near edge structure (XANES) spectroscopic at the sulfur K-edge with synchrotron radiation by beamline 8 at Synchrotron Light Research Institute (Public Organization). The peak shift is reported to be related to the number of sulfur atoms within the sulfur crosslink [50-51], whilst the absorption peak of the XANES spectrum is shifted to a lower photon energy when the number of sulfur atoms is increased. The K-edge XANES spectrum of the sulfur atom is characterized by an absorption line at ~2472 eV varying with its local geometric and electronic environment. Based on this, XANES was used here to qualitatively investigate the changes of the sulfur crosslink distribution with respect to curing time.

#### 4.3.1 Sulfur Crosslink Distribution of Gum NR Vulcanizates

The changes in the overall sulfur crosslink distribution of gum NR vulcanizates cured with different cure times as follow  $tc_{50}$ ,  $tc_{60}$ ,  $tc_{70}$ ,  $tc_{80}$ ,  $tc_{90}$ ,  $tc_{100}$  and  $tc_{100+20\text{ min}}$  were focused in this part. Figure 4.37 shows XANES spectra of gum NR vulcanizates cured at 160°C with different curing times. There were two characteristics of peak concerned. The first one was the area of peak relating to the total crosslinks. The second one was the position of peak relating to the sulfur crosslink distribution. It can be seen that when increasing curing time from  $tc_{50}$  to  $tc_{70}$ , the position of peak gradually shifted to the lower energy. The XANES of the gum NR vulcanizate cured with  $tc_{70}$  appeared at the lowest energy with the highest peak area. The might be inferred that the second step of vulcanization proposed by Krejsa and Koenig [67] was terminated at this curing time,  $tc_{70}$ . After this point, there was only the maturing reaction of the polysulfidic crosslinks. When further increasing curing time from  $tc_{70}$  to  $tc_{100}$ , the peak now shifted to the higher energy with lower peak area. This indicated the desulfuration and decomposition of the polysulfidic crosslinks. When the compound was over-cured,  $tc_{100+20\text{ min}}$ , the peak area obviously decreased and its position shifted to even higher energy. The occurrence of the peak at higher energy of the over-cured vulcanizates was due to the extensive

decomposition of polysulfidic crosslinks. Now the over-cured vulcanizate consisted mainly of mono- or disulfidic crosslinks responding to the higher energy position. The results here indicated that XANES study showed the good sensitivity of the spectra to the overall sulfur crosslink distribution with respect to the curing times.

Figure 4.38 shows the comparison of XANES spectra between the gum vulcanizates cured at 160 and 180°C using  $t_{c_{100+20 \text{ min}}}$ . As mentioned in section 4.1.2, using high curing temperature caused the gum vulcanizate to undergo more reversion. The result in Figure 4.41 also supported this. As can be seen, the peak of the gum vulcanizates cured at 180°C was located at the higher energy. It meant most of polysulfidic crosslinks formed earlier decomposed much easier. Therefore, only mono- and disulfidic crosslinks were left in the networks.

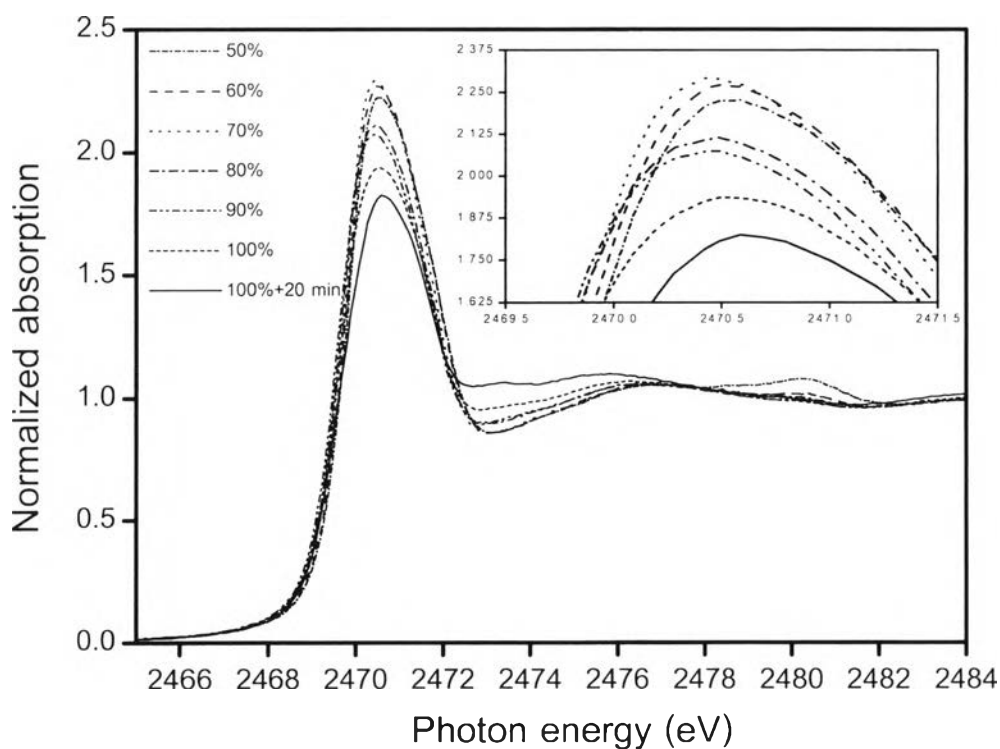


Figure 4.37 XANES spectra of gum NR vulcanizates cured at 160°C with various curing times

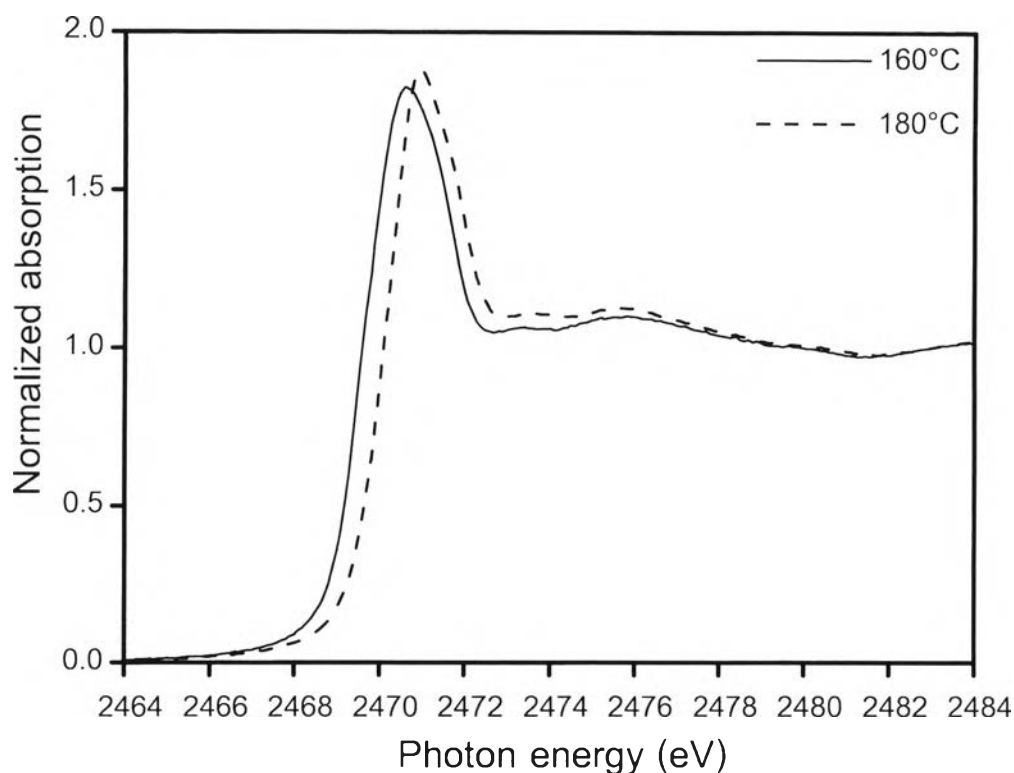


Figure 4.38 XANES spectra of gum NR vulcanizates cured with  $tc_{100+20 \text{ min}}$

#### 4.3.2 Sulfur Crosslink Distribution of Carbon Black filled NR Vulcanizates

The XANES spectra of the N330 filled NR vulcanizates cured with different cure times as follow  $tc_{50}$ ,  $tc_{60}$ ,  $tc_{70}$ ,  $tc_{80}$ ,  $tc_{90}$ ,  $tc_{100}$  and  $tc_{100+20 \text{ min}}$  are shown in Figure 4.39. The carbon black loading was fixed at 40 phr. The changes in the overall sulfur crosslink distribution of the N330 filled NR vulcanizates over different curing times were focused. First of all, it was observed that even using the same DCBS accelerated cure system, the presence of 40 phr N330 significantly affected on the shifting of peaks as a function cure times. Moreover, the peak of the N330 filled vulcanizate was much broader than that of the gum one. However, similar to the gum vulcanizate, the peak of the N330 filled NR vulcanizate cured with  $tc_{70}$  also located at the lowest energy. Increasing curing time from  $tc_{70}$  to  $tc_{100}$  caused the peaks move to the higher energy. This indicated the maturing reaction of polysulfidic linkages. The crosslinks with shorter sulfur ranks were formed. When the N330 filled NR vulcanizate was overcured, most of crosslink structures left in the networks were mono- and disulfidic linkages, thus giving the peak at highest energy.

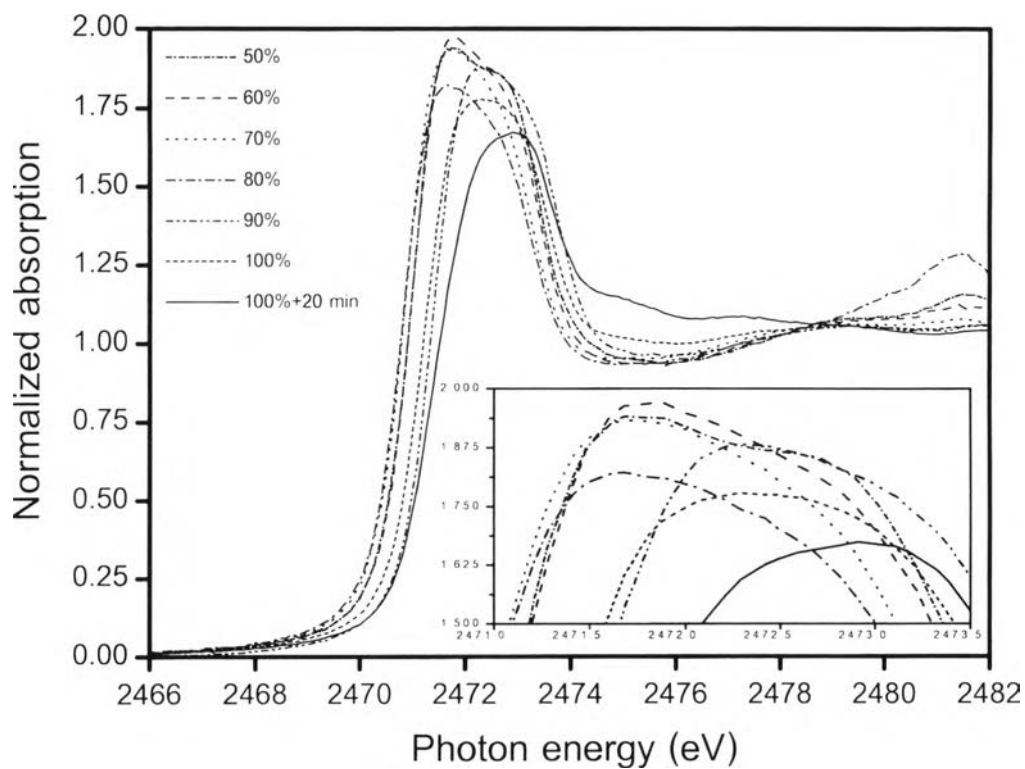


Figure 4.39 XANES spectra of 40 phr N330 filled NR vulcanizates cured at 160°C with various curing times

The XANES spectra of the N550 filled NR vulcanizates cured with different cure times as follow  $tc_{50}$ ,  $tc_{60}$ ,  $tc_{70}$ ,  $tc_{80}$ ,  $tc_{90}$ ,  $tc_{100}$  and  $tc_{100+20 \text{ min}}$  are shown in Figure 4.40. The carbon black loading was fixed at 50 phr. The changes in the overall sulfur crosslink distribution of the N550 filled NR vulcanizates over different curing times were focused. The shift of peak with respect to curing time also observed. However, the shifting of peak of the NR vulcanizates filled with N550 was much less than that of the one filled with N330. This might be due to the lower reversion of vulcanizates filled with N550.

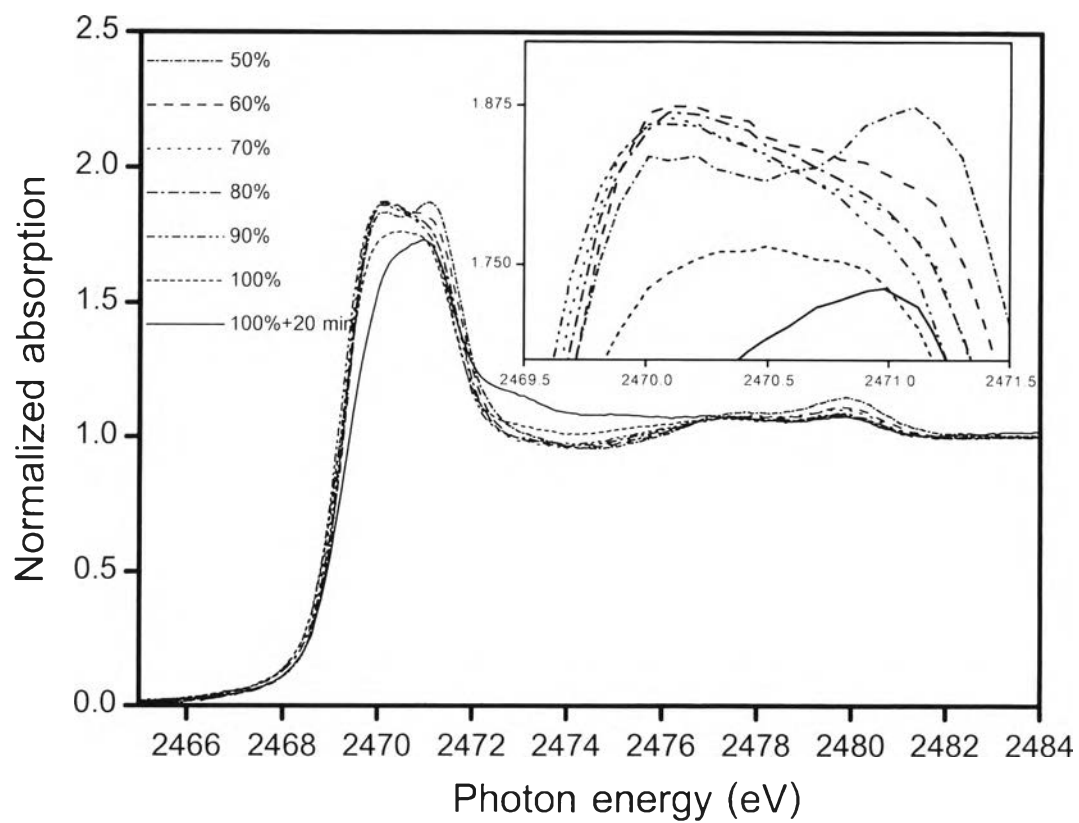


Figure 4.40 XANES spectra of 50 phr N550 filled NR vulcanizates cured at 160°C with various curing times

#### 4.4 Characterization of Graphitized Carbon Black

The N330 was treated by high temperature (1700°C) under nitrogen atmosphere to study effect of surface activity on the cure characteristics, reversion behavior and thermal aging properties of the NR compounds. So in this part, the change in crystallinity of N330 carbon black before and after graphitization was characterized using an X-ray diffractometer (XRD). The X-ray diffraction patterns for N330 before and after high temperature treatment are shown in Figure 4.41.

The result shown in Figure 4.44 indicated that N330 gave broad peak while gN330 showed sharp peak at  $2\theta$  values of  $26.2^\circ$ . It was apparent gN330 exhibited the higher crystallinity than N330 did. This was because during heat treatment size of the nanocrystallites, drastically increased and the arrangement of these crystallites became more ordered. As a consequence the microstructure was totally changed, the number of high energy sites, located at the edges of the crystallites, decreases drastically. This confirmed the assumption that the surface activity of carbon blacks also played an important role on the cure characteristic of the NR compound observed in the section 4.2.



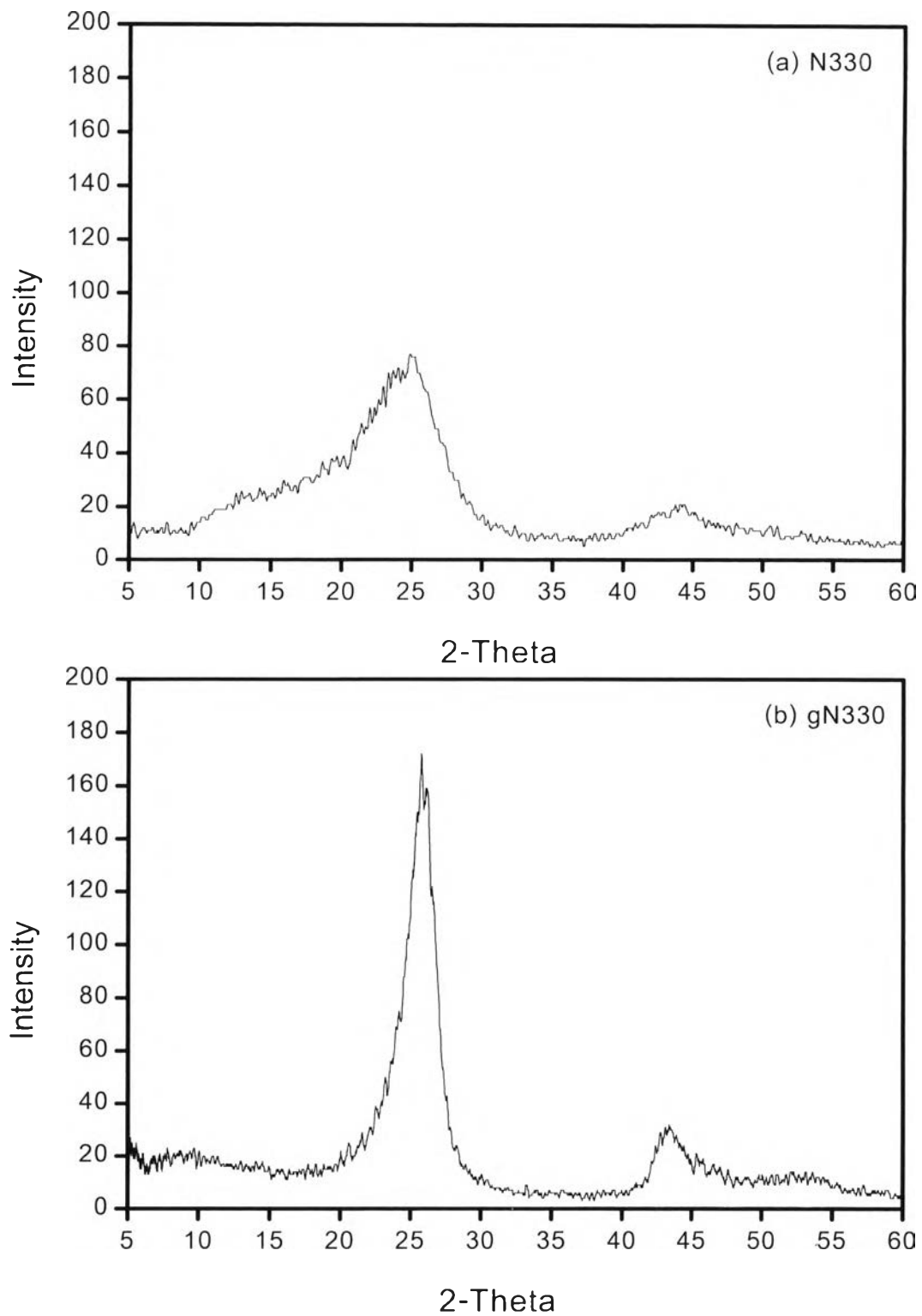


Figure 4.41 XRD patterns for (a) N330 and (b) gN330