Table Captions

Table 1	Carbon black properties
Table 2	Compounding ingredients used in the present study

Figure Captions

Figure 1 Storage modulus (G′) as a function of strain amplitude of cured HNBR specimens (vulcanisates) with various N326 loadings (measured at 1 rad/s and 60°C)

Figure 2 Loss modulus (G″) as a function of strain amplitude of cured HNBR specimens (vulcanisates) with various N326 loadings (measured at 1 rad/s and 60°C)

Figure 3 Damping factor (tanδ) as a function of strain amplitude of cured HNBR specimens (vulcanisates) with various N326 loadings (measured at 1 rad/s and 60°C)

Figure 4 Storage modulus (G′) as a function of strain amplitude of cured HNBR specimens (vulcanisates) with various carbon black surface areas (measured at 1 rad/s and 60°C)

Figure 5 Cure curves of HNBR vulcanisates filled with various types of carbon black

Figure 6 Loss modulus (G″) as a function of strain amplitude of cured HNBR specimens (vulcanisates) with various carbon black surface area (measured at 1 rad/s and 60°C)

Figure 7 Damping factor (tanδ) as a function of strain amplitude of cured HNBR specimens (vulcanisates) with various carbon black surface area (measured at 1 rad/s and 60°C)

Figure 8	Relationship among heat build-up (HBU), carbon black loading and surface area of HNBR vulcanisates
Figure 9	Relationship between heat build-up (HBU) and loss modulus (G″) measured at 10 %strain and 60°C of cured HNBR (vulcanisates) with various carbon black surface areas and loadings: 20 phr (black solid symbol); 40 phr (gray solid symbol); 60 phr (unfilled symbol)
Figure 10	Relationship between heat build-up (HBU) and damping factor (tanδ) measured at 10 %strain and 60°C of cured HNBR (vulcanisates) with various carbon black surface areas and loadings: (black solid symbol) 20 phr; (gray solid symbol) 40 phr; (unfilled symbol) 60 phr

Table 1 Carbon black properties

Table 1 Carbon black properties

Properties	N326	N550	N774	N990
Iodine Adsorption No. D 1510 (g/kg)	82	43	29	-
DBP No. D 2414 (10^{-5} m^3/kg)	72	121	72	43

Table 2 Compounding ingredients used in the present study

Table 2 Compounding ingredients used in the present study

Chemical name	Function	Amount (phr)
HNBR	Rubber matrix	100
Carbon black	Reinforcing filler	varied: 0-60
TMQ[a]	Antioxidant	1
Zinc Oxide (ZnO)	Cure activator/Filler	5
Stearic acid	Cure activator/Softener	1
TOTM[b]	Plasticizer	5
Dicumyl peroxide (DCP)	Curing agent	2

[a] 2, 2, 4-trimethyl-1, 2-dihydroquinoline

[b] tri-2-ethylhexyl trimellitate

Figure 1

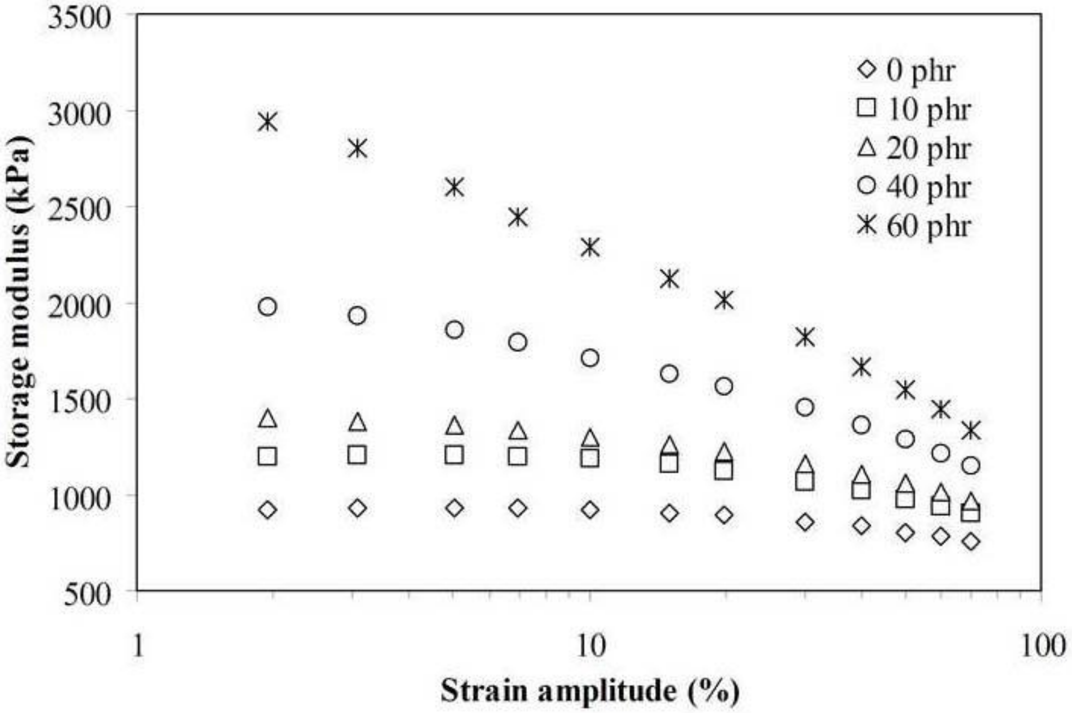

3500
3000
2500
2000
1500
1000
500
Storage modulus (kPa)
1
10
100
Strain amplitude (%)
◇ 0 phr
□ 10 phr
△ 20 phr
○ 40 phr
✳ 60 phr

Figure 2

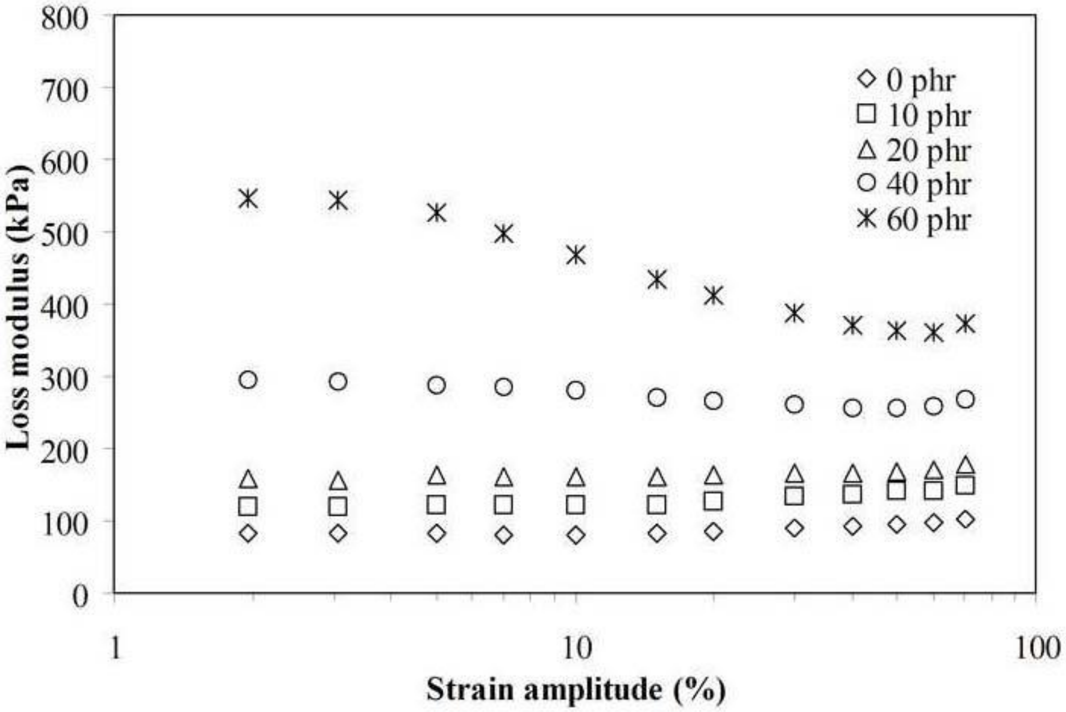

Loss modulus (kPa)
0
100
200
300
400
500
600
700
800
1
10
100
Strain amplitude (%)
◇ 0 phr
□ 10 phr
△ 20 phr
○ 40 phr
✳ 60 phr

Figure 3

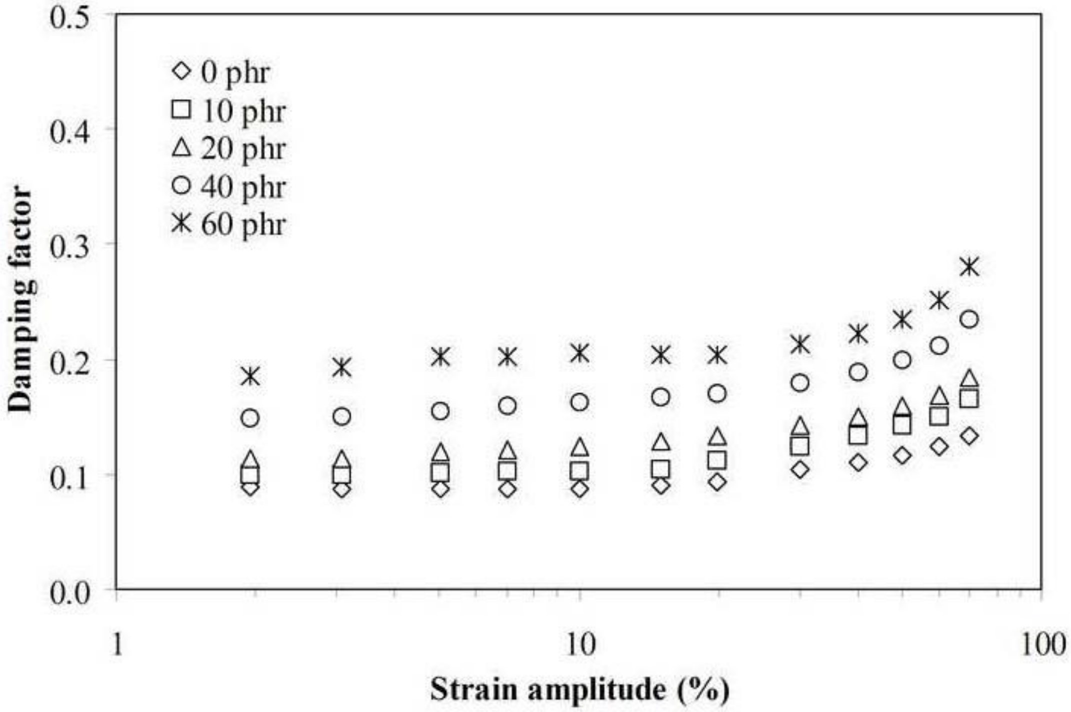

◇ 0 phr
□ 10 phr
△ 20 phr
○ 40 phr
✳ 60 phr
Damping factor
0.0
0.1
0.2
0.3
0.4
0.5
1
10
100
Strain amplitude (%)

Figure 4

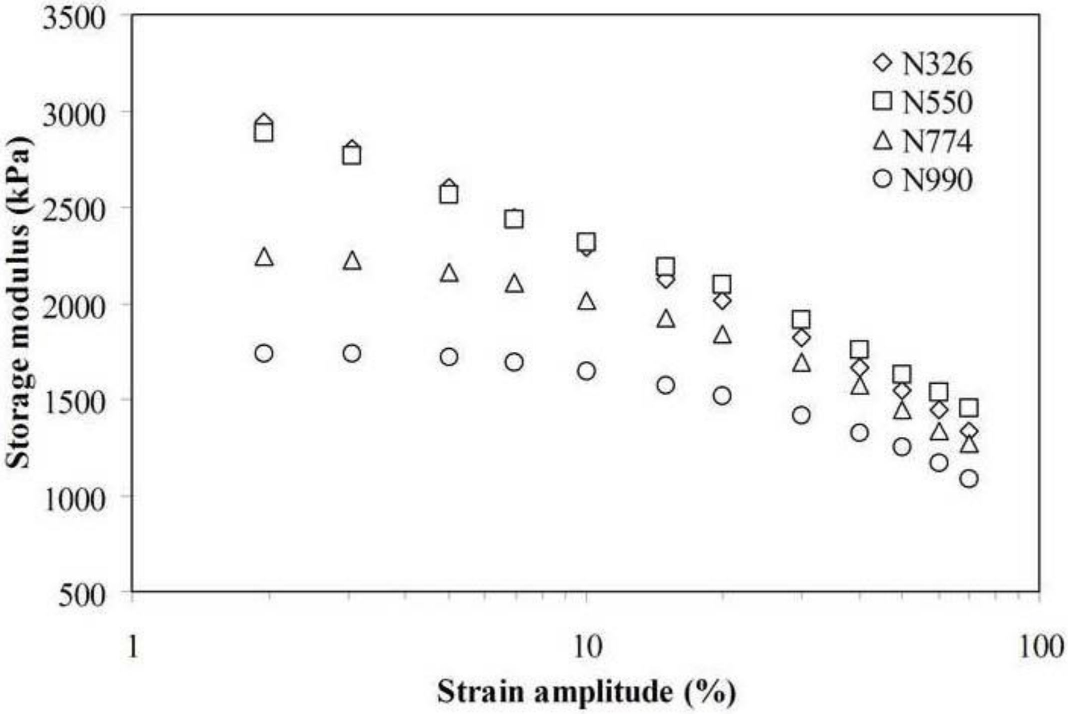

3500
3000
2500
2000
1500
1000
500
Storage modulus (kPa)
1
10
100
Strain amplitude (%)
◇ N326
□ N550
△ N774
○ N990

Figure 5

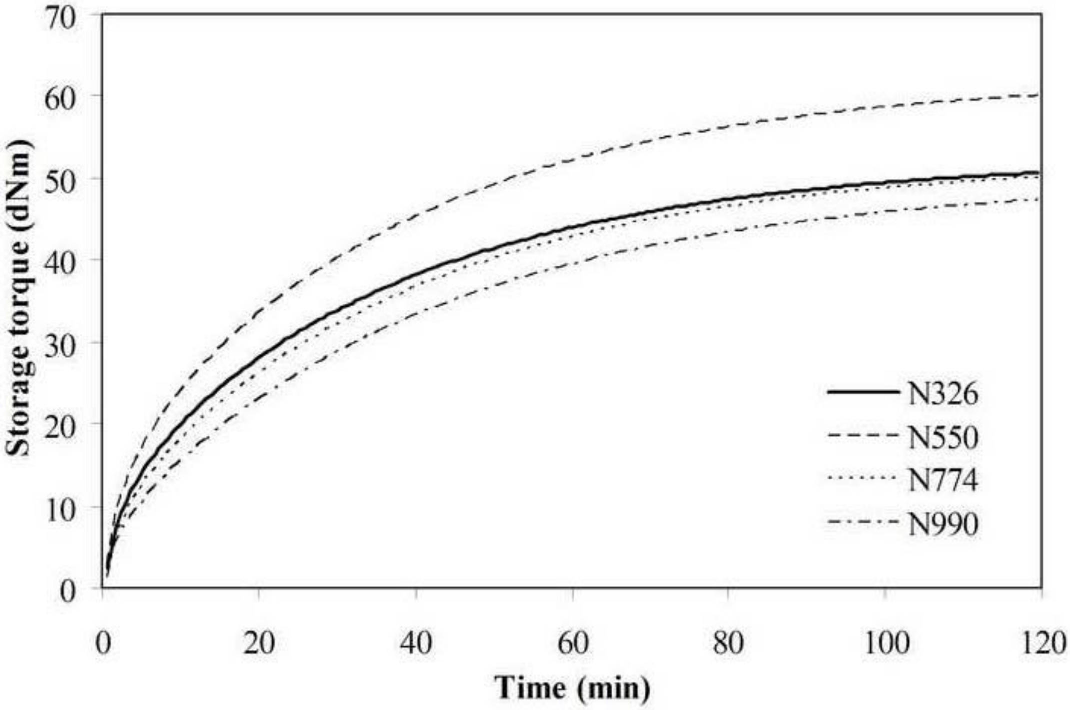

Storage torque (dNm)
0
10
20
30
40
50
60
70
Time (min)
0
20
40
60
80
100
120
N326
N550
N774
N990

Figure 6

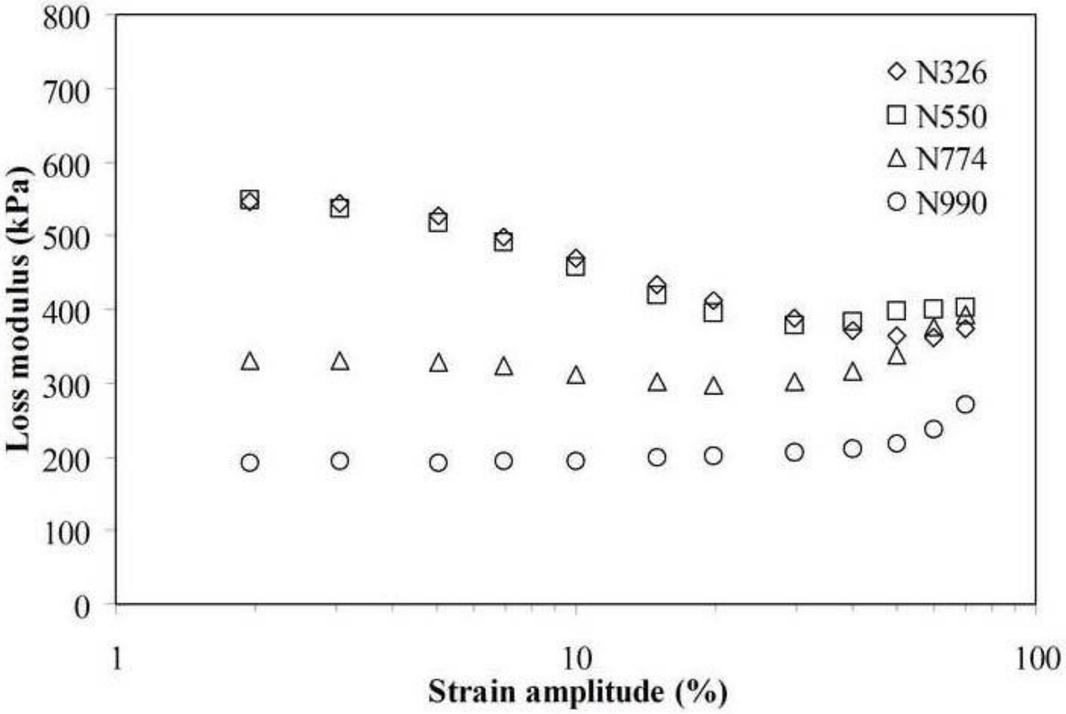

Loss modulus (kPa)
0
100
200
300
400
500
600
700
800
Strain amplitude (%)
1
10
100
◇ N326
□ N550
△ N774
○ N990

Figure 7

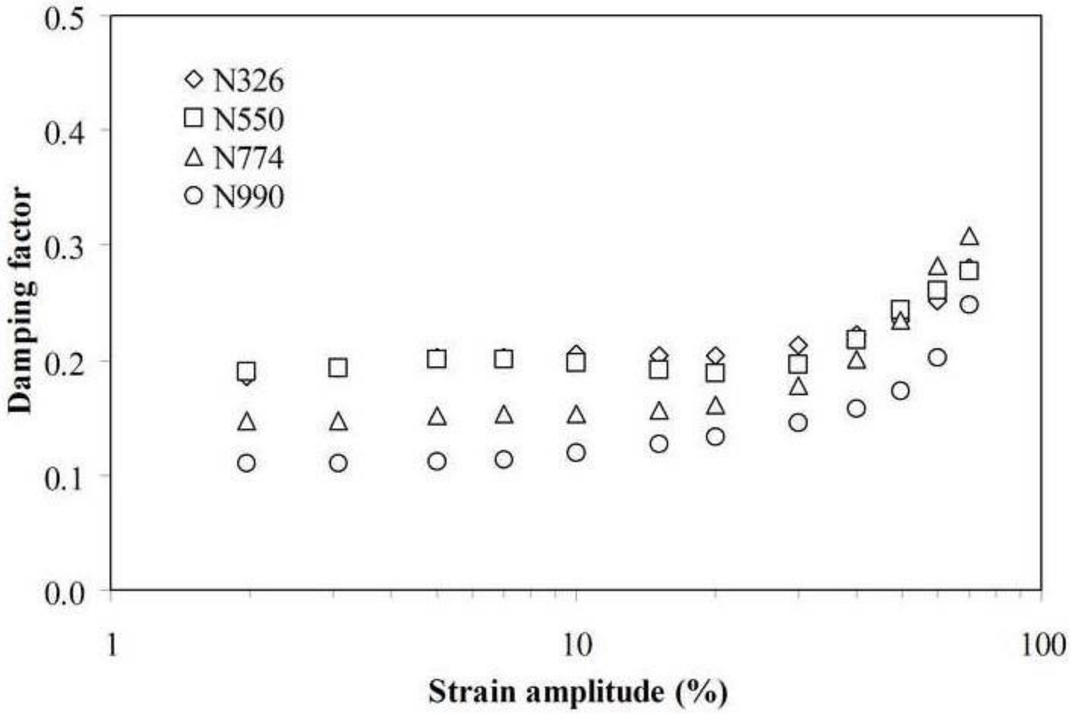

0.5
0.4
0.3
0.2
0.1
0.0
Damping factor
◇ N326
□ N550
△ N774
○ N990
1
10
100
Strain amplitude (%)

Figure 8

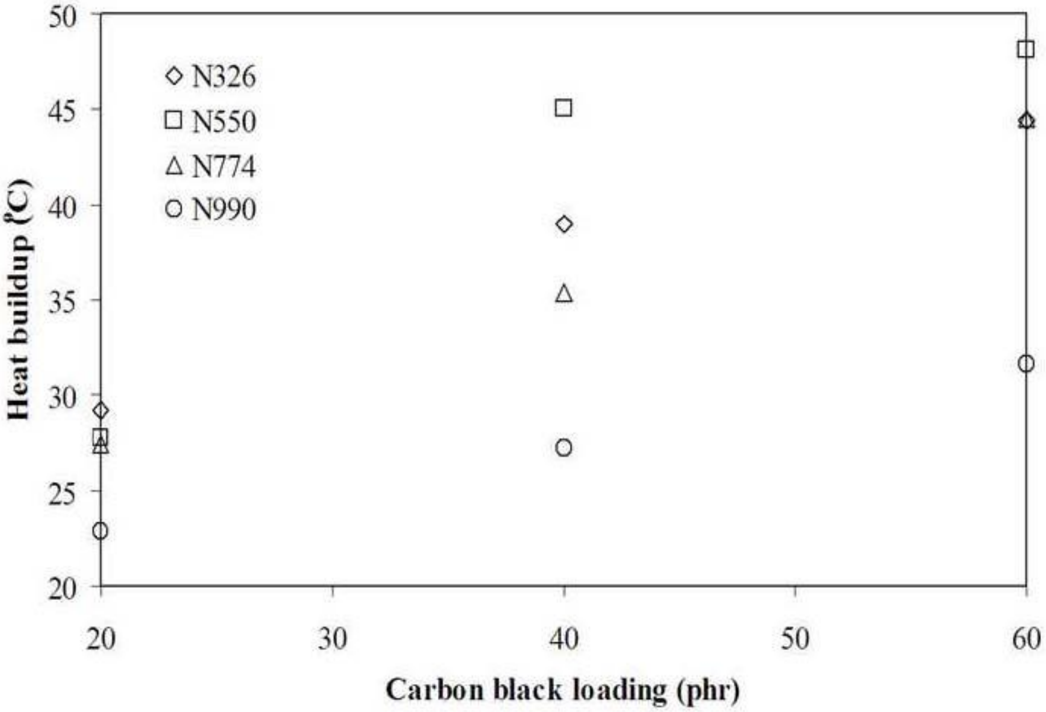

◇ N326
□ N550
△ N774
○ N990
Heat buildup (°C)
50
45
40
35
30
25
20
Carbon black loading (phr)
20
30
40
50
60

Figure 9

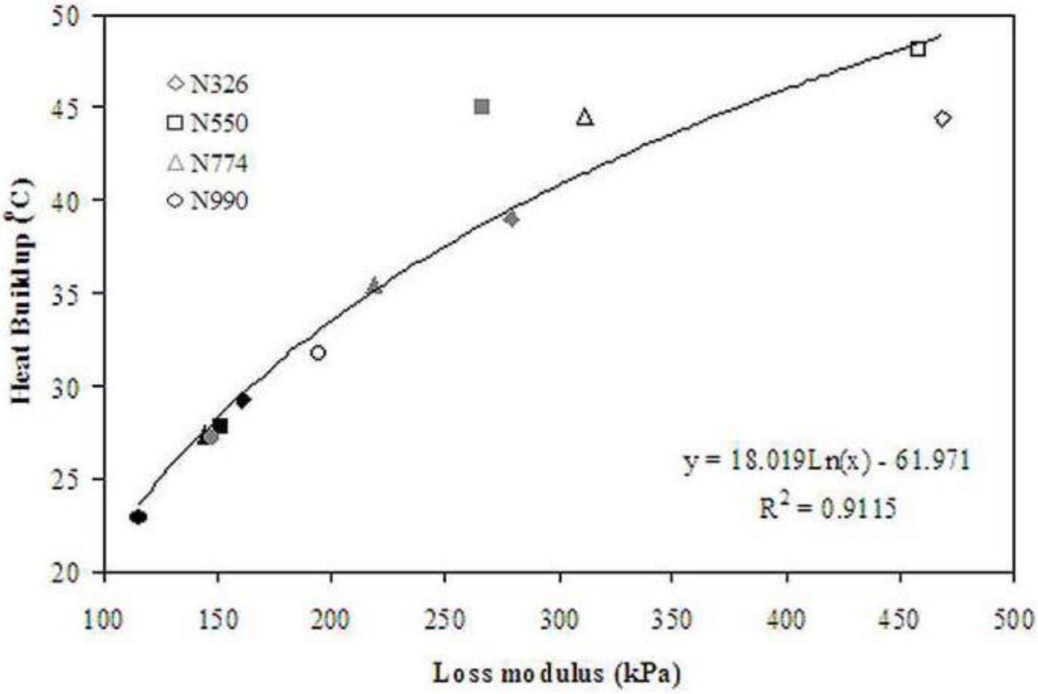
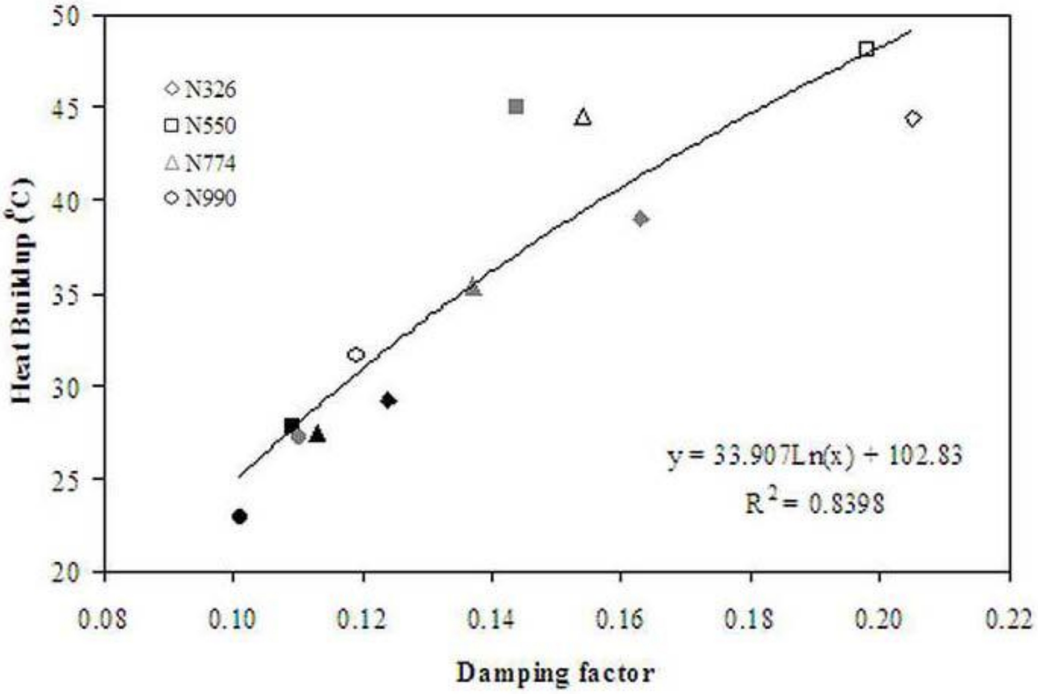

◇ N326
□ N550
△ N774
○ N990
y = 18.019Ln(x) - 61.971
R^2 = 0.9115
Heat Buildup (°C)
Loss modulus (kPa)
50
45
40
35
30
25
20
100
150
200
250
300
350
400
450
500

Figure 10



◇ N326
□ N550
△ N774
○ N990
y = 33.907Ln(x) + 102.83
R² = 0.8398
Heat Buildup (°C)
Damping factor
50
45
40
35
30
25
20
0.08
0.10
0.12
0.14
0.16
0.18
0.20
0.22

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Kautschuk & Gummi-Kunststoffe

Cure and Viscoelastic Properties of HNBR

Effects of Carbon Black

Reinforcement · Viscoelastic properties · Carbon black · Cynamic mechanical properties · Hydrogenated acrylonitrile butadiene rubber

Cure, viscoelastic and mechanical properties of HNBR filled with various types of carbon black were investigated. By increasing carbon black loading and specific surface area, cure promotion was observed which could be explained by a combination of thermal history, surface chemistry and thermal conductivity. Viscoelastic behaviour of both uncured and cured specimens filled with carbon black exhibits a strain-dependent behaviour. Storage modulus (G') and damping factor ($\tan\delta$) significantly increase with increasing carbon black loading and/or specific surface area. Mechanical properties are found to be governed by combined effects associated with carbon black dispersion. The overall results imply a close correlation of viscoelastic and mechanical properties via energy dissipation process (or hysteretic process) caused by molecular slippage.

Vernetzung und viskoelastische Eigenschaften von HNBR: Einfluss von Ruß

Verstärkung · viskoelastische Eigenschaften · Ruß · dynamisch-mechanische Eigenschaften · hydrierter Acrylnitril-Butadien Kautschuk

Das Vernetzungsverhalten und mechanische Eigenschaften von rußgefülltem HNBR wurden untersucht. Durch die Erhöhung der Dosierung sowie der spezifischen Oberfläche des Rußes wurde eine Verkürzung der Heizzeit hervorgerufen, die der thermischen Vorgeschichte, der Oberflächenchemie und der thermischen Leitfähigkeit zugeordnet wird. Die viskoelastischen Eigenschaften sowohl der nichtvernetzten als auch der vernetzten Proben zeigen eine ausgeprägte Amplitudenabhängigkeit. Der Speichermodul (G') und der Dämpfungsfaktor ($\tan\delta$) steigen signifikant mit der Dosierung und der spezifischen Oberfläche der Ruße an. Es wird gezeigt, dass die mechanischen Eigenschaften der Vulkanisate von der Rußdispersion beeinflusst werden und eine Korrelation zwischen viskoelastischen und mechanischen Eigenschaften besteht, die durch dissipatorische Prozesse erklärt wird.

Figures and Tables:
By a kind approval of the authors

Hydrogenated acrylonitrile butadiene rubber (HNBR), as a synthetic rubber produced by the hydrogenation reaction of nitrile rubber (NBR), possesses excellent oil and thermal resistance. Typically, HNBR has widely been employed in automotive and industrial applications [1, 2]. HNBR is known to be curable with either peroxide or sulfur/sulfur-donor cure systems, depending on its degree of unsaturation on the backbone as well as on product properties required. Laboratory comparisons of sulfur/sulfur-donor and peroxide cured HNBR compounds reveal that the peroxide vulcanisation provides superior compression set and heat resistance [1]. Although HNBR offers relatively good mechanical properties due to its highly saturated structure facilitating the molecular packing, an incorporation of filler into HNBR is still necessary for further enhancing mechanical and dynamic properties and well as performance per cost of the final products [3, 4]. The reinforcement performance of filler has been reported to depend typically on filler characteristics including specific surface area, surface chemistry and structure (or degree of aggregation) [5-7]. In general, the greater loading of reinforcing will result in the higher hardness and modulus [8-11]. Simultaneously, property improvement and processability are found to reach its maxima at certain filler loading relying on the mixing efficiency for filler dispersion and distribution (i.e., state-of-mix) [2]. There are numerous works on enhancement in mechanical properties of HNBR vulcanisates by reinforcing fillers including carbon black [12-14], silica [13-15], carbon nanotubes [14-17] and organoclay [18-20]. Nonetheless, published work on viscoelastic properties of carbon black filled HNBR is still limited. It is reported that storage modulus (G') increases and damping factor peak ($\tan\delta_{max}$) decreases with carbon black loading which is attributed to the changes in occluded rubber, bound rubber and shell rubber [21, 22]. By increasing carbon black specific surface area, the $\tan\delta$ appears to decrease in the transition zone and then increase in the plateau zone (rubber plateau). The magnitude of G' enhancement is more obvious with increasing specific surface area of carbon black. However, the comparison of viscoelastic properties between uncured and cured HNBR filled with carbon black have not yet been reported. Therefore, the present work aims to investigate viscoelastic behaviour and mechanical properties of HNBR filled with carbon black having different specific surface areas and structures.

Experimental

Materials

Raw HNBR (Therban VP KA 8837) having acrylonitrile and unsaturation contents of 34% and 18%, respectively, used in this study was supplied by Lanxess Co., Ltd. (Bangkok, Thailand). Four grades of carbon blacks (CBs) (i.e., N326, N550, N774 and N990) were supplied by Loxley Public Co., Ltd. (Bangkok, Thailand) and Siam Luck Trading Co., Ltd. (Bangkok, Thailand). The characteristics are given in Table 1. [23]. Tri-2-ethylhexyl trimellitate (TOTM) as plasticizer was purchased from Behn Meyer Chemical (Thailand) Co., Ltd. (Bangkok Thailand). Dicumyl peroxide or DCP (98% active) as curing agent was supplied by Petchthai Chemical Co., Ltd (Bangkok, Thailand).

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Sample Preparation

Mixing was performed on a laboratory size two roll mill (LabTech Co., Ltd., Bangkok, Thailand) at set temperature of 40 °C. HNBR and compounding ingredients as shown in Table 2 were mixed for 20 minutes. HNBR vulcanisate sheets were prepared using a hot-press at a temperature of 145 °C under moulding pressure of 150 kg/cm² for 120 minutes.

Test procedures

Cure characteristics Cure characteristics were monitored at 145 °C using the Rubber Process Analyser (RPA2000, Alpha Technologies, USA) with test frequency and strain of 6.28 rad/s and 15 %, respectively. Scorch time (t_{s2}) was determined from time to achieve torque rise of 2 units above the minimum torque. Cure time used in the present work was the time to reach 90 % complete cure state (t_{c90}). Torque difference between the maximum and minimum storage torques ($\Delta S'$) was used as an indication of crosslink density [24].

Viscoelastic properties Rubber Process Analyser (RPA2000, Alpha Technologies, USA) was used for viscoelastic behaviour measurement of HNBR compounds and vulcanisates. Strain sweep test was performed at test temperatures of 100 °C and 60 °C for measuring dynamic properties of uncured and cured HNBR, respectively.

Mechanical properties The universal tensile tester (Instron model 5566, USA) was used for measuring the tensile properties as per ASTM D412-98 at a crosshead speed of 500 mm/min [25]. Test specimens for tensile were punched out from the moulded sheets using ASTM die C. Hardness test was performed on 6-mm-thick specimen using with a hardness durometer (Wallace H177A, UK) at room temperature as per ASTM D2240-97 [26]. Abrasion resistance of HNBR vulcanisates was measured using the DIN-type abrasion tester (Zwick model 6120, Germany) in accordance with DIN 53516 [27].

Result and Discussion

Cure characteristics

Results of scorch time (t_{s2}), time for 90 % of cure completion (t_{c90}) and the difference between the maximum and minimum torques ($\Delta S'$) -an indication of crosslink density [24]- are presented in Table 3. It becomes evident that both the scorch time (t_{s2}) and the cure time (t_{c90}) decrease while torque difference increases as a function of CB loading. These results imply clearly a cure promotion phenomenon by the incorporation of CB. The explanations are postulated by: (i) the thermal history, (ii) the alkalinity of CB and (iii) the high thermal conductivity of CB.

1 Carbon black properties [23]

Properties	N326	N550	N774	N990
Iodine Adsorption No. D 1510 (g/kg)	82	43	29	-
DBP No. D 2414 (10^{-5} m³/kg)	72	121	72	43

2 Compounding formulation used

Chemical name	Amount (phr)
HNBR	100
Carbon black	varied: 0-60
TMQ[a]	1
Zinc Oxide (ZnO)	5
Stearic acid	1
TOTM[b]	5
Dicumyl peroxide (DCP)	2

[a] 2, 2, 4-trimethyl-1, 2-dihydroquinoline
[b] tri-2-ethylhexyl trimellitate

It has been known that, as filler loading increases, bulk viscosity increases with the magnitude depending on filler specific surface area and filler-rubber interaction. This would lead to a rise in bulk temperature via shear heating and thus to an influence on the thermal history applied to the rubber bulk. By this means, the high magnitude of thermal history experienced in compound leads to an acceleration of curative dissociation in compounds and eventually in formation of crosslink precursors.

Regarding the pH of CB surfaces it is known that to some degree alkalinity is present and can promote the functioning of curatives [28]. In terms of thermal conductivity effect, compared with raw rubber, carbon black as solid particles possesses much higher thermal conductivity (0.1-0.6 W/mK for rubber [29] and ~2 W/mK for CB [30]) which helps transferring heat from mould surface to rubber, if a three-dimensional filler network is formed.

However, it is evident that, at any given carbon black loading, the specific surface area of carbon black affects cure behaviour to some extent, but with the lower magnitude than the carbon black loading. Exceptionally, the crosslink density appears to be highest in HNBR with CB N550 [31]. It is proposed that the tightly bound rubber in CB N550 with more developed structure obstructs curative absorption on carbon black surfaces, leading to the increase in free curatives migrating to the free rubber matrix a migration of, and the crosslinking reaction in rubber bulk is thus promoted [31].

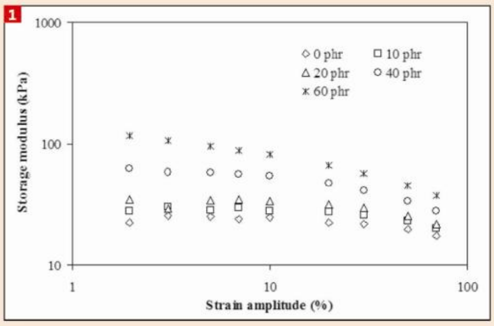
Viscoelastic properties

Effect of carbon black loading Uncured HNBR compounds The effect of carbon black loading on dynamic mechanical properties of uncured compounds with various carbon black loadings are shown in Figures 1 to 3. Figure 1 shows plots of G' meas-

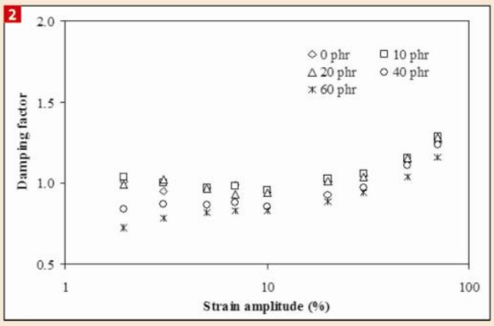
3 Cure characteristics of HNBR and filled HNBR

Carbon black	Loading (phr)	t_{s2} (min)	t_{c90} (min)	S'max-S'min[a] (dNm)
Control	0	1.42±0.03	74.54±1.07	28.14±0.19
CB N326	10	1.30±0.03	74.73±0.37	31.57±0.72
	20	1.17±0.01	73.94±0.50	36.35±0.09
	40	1.06±0.01	71.94±0.31	42.61±0.71
	60	0.98±0.03	69.22±0.20	48.71±1.21
CB N550	10	1.21±0.15	74.06±0.76	34.02±0.18
	20	1.10±0.06	73.93±0.39	38.11±0.55
	40	0.98±0.05	72.14±0.88	49.61±0.60
	60	0.87±0.04	69.86±1.96	54.77±3.21
CB N774	10	1.33±0.03	74.25±1.42	32.32±1.91
	20	1.20±0.02	74.07±1.18	37.73±0.81
	40	1.06±0.03	72.65±1.59	43.43±2.91
	60	0.99±0.02	71.44±1.25	46.51±2.84
CB N990	10	1.21±0.15	75.23±0.06	32.54±0.80
	20	1.22±0.03	75.83±0.16	35.47±0.20
	40	1.12±0.02	75.48±0.09	41.13±0.44
	60	1.06±0.04	75.69±0.70	45.47±0.77

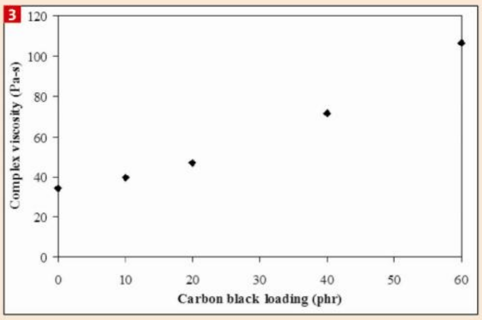
a = Torque difference between maximum (S'max) and minimum torques (S'min) as determined from cure curves



1 Storage modulus (G') as a function of strain amplitude of uncured HNBR compounds with various CB N326 loadings (measured at 1 rad/s and 100 °C)



2 Damping factor (tanδ) as a function of strain amplitude of uncured HNBR compounds with various CB N326 loadings (measured at 1 rad/s and 100 °C)



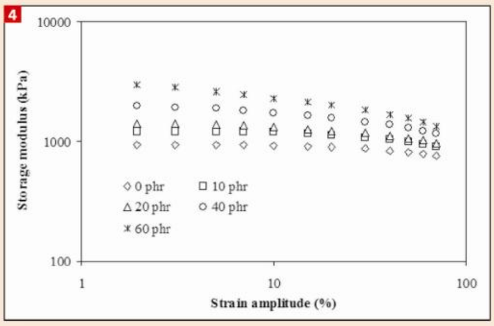
3 Complex viscosity (η*) of uncured HNBR compounds as a function of CB N326 loading (measured at 1 rad/s, 10 % strain and 100 °C)

ured at 60 °C against strain amplitude (%) of HNBR compounds filled with different loadings of CB N326 carbon black. Clearly, at low strain, G' of unfilled compound is lowest, while the G' of filled compound with CB of 60 phr is highest. The G' of filled blend increases with increasing CB loading, which is due mainly to reinforcing effect, i.e., the hydrodynamic effect, the filler-filler interaction as well as the CB -HNBR interaction [32,33]. Moreover, it is evident that the compounds show relatively broad linear viscoelastic (LVE) region until the CB loading up to 20 phr, and then the blends with CB loading of 40 phr show narrow LVE region. The compound with CB loading of 60 phr shows no significant LVE region. The decrease in LVE region is associated with an increase in G', indicating an increase in magnitude of filler network formation (Payne effect) [33]. At high CB loading, the magnitude of filler network is high, which would be disrupted at high shear strain. This is the reason why the LVE of highly filled blends could not be observed.

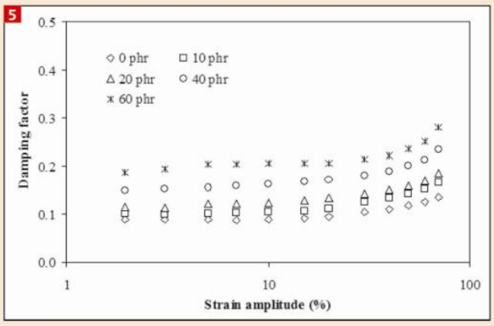
4 **Mechanical properties of filled HNBR vulcanisates**

Carbon black	Loading (phr)	M100 (MPa)	Tensile strength (MPa)	Elongation at break (%)	Hardness (shore A)	Abrasion loss (mm³)
Control	0	2.16±0.05	9.48±0.21	252.98±5.54	59.6±0.2	54.43±2.97
CB N326	10	3.13±0.23	13.92±0.79	259.08±13.08	63.7±0.17	62.08±1.73
	20	3.77±0.23	16.39±0.34	250.08±8.82	68.5±0.1	64.96±1.48
	40	7.00±0.72	18.96±1.49	205.10±17.56	76.0±0.23	67.77±1.58
	60	10.13±0.11	19.30±0.34	168.20±3.01	81.7±0.46	86.16±1.18
CB N774	10	3.16±0.19	14.45±0.16	259.36±6.92	65.2±0.25	57.33±2.12
	20	4.21±0.16	16.15±0.62	227.55±3.11	69.4±0.30	58.14±1.74
	40	7.12±0.06	17.55±0.36	165.47±11.79	77.0±0.25	61.90±1.13
	60	12.00±0.83	18.04±0.86	136.27±2.57	81.9±0.42	71.66±1.11
CB N550	10	2.73±0.13	9.62±0.46	219.18±8.18	63.5±0.32	67.75±3.52
	20	4.04±0.28	15.69±0.16	232.93±7.97	68.2±0.10	68.51±4.57
	40	6.14±0.34	18.11±0.55	204.44±9.36	74.4±0.40	64.11±0.58
	60	10.08±0.70	20.92±1.11	182.79±9.96	78.7±0.46	70.99±0.75
CB N990	10	2.52±0.18	10.62±0.25	244.63±9.66	62.2±0.38	60.82±1.27
	20	3.08±0.21	11.19±0.51	220.84±10.08	64.4±0.12	67.53±1.79
	40	4.23±0.61	13.44±0.10	206.25±18.66	68.8±0.15	72.50±1.44
	60	5.48±0.28	17.35±0.31	218.73±7.94	72.8±0.55	81.84±0.67

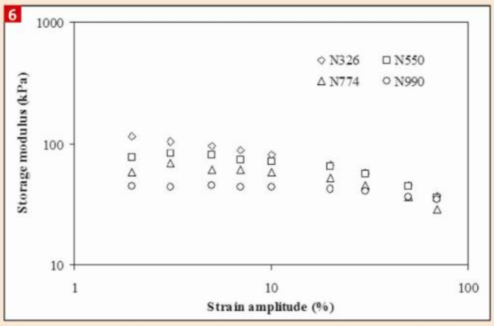
Results of damping factor (tanδ) are shown in Figure 2. It is obvious that the damping factor of all compounds increases with increasing strain amplitude. This is due to the energy dissipation through a molecular slippage associated with the breakdown of the three-dimensional filler transient network. This phenomenon is sometimes interpreted as a hysteretic process [32]. Notably, the damping factor of unfilled compounds is highest, and decreases with increasing carbon black loading particularly at low shear strain. The low values for tan δ is related to the fact that the storage modulus of the compound increases more than the loss modulus. Furthermore, the formation of three-dimensional transient filler network is responsible for the rise in elastic contribution. From another perspective, the damping behaviour of highly filled compounds at low strain could be explained by the dilution of the viscoelastic contribution of rubber matrix by as a fully elastic component



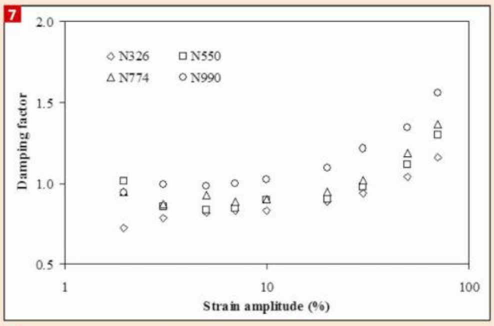
4 Storage modulus (G') as a function of strain amplitude of cured HNBR specimens (vulcanisates) with various CB N326 loadings (measured at 1 rad/s and 60 °C)



5 Damping factor (tanδ) as a function of strain amplitude of cured HNBR specimens (vulcanisates) with various CB N326 loadings (measured at 1 rad/s and 60 °C)



6 Storage modulus (G') as a function of strain amplitude of uncured HNBR compounds with various carbon black specific surface area (measured at 1 rad/s and 100 °C)



7 Damping factor (tanδ) as a function of strain amplitude of uncured HNBR compounds with various carbon black specific surface area (measured at 1 rad/s and 100 °C)

by carbon black particles having a damping factor approaching zero.

The processability of HNBR was monitored in terms of complex viscosity (η*), as shown in Figure 3. It is obvious that η* increases with carbon black loading which is in good agreement with the filler reinforcement effect. In other words, the processability appears to decrease due to the hydrodynamic reinforcement, i.e. (i) flow obstruction caused by solid filler particles, (ii) strong rubber-filler interactions and (iii) a formation of three-dimensional transient filler network.

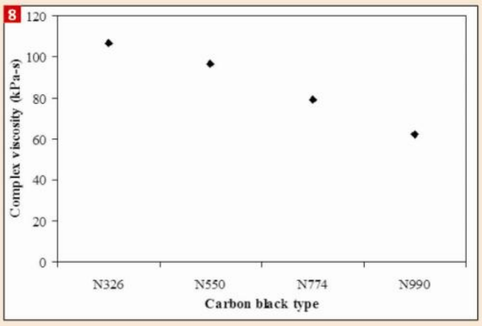
Cured HNBR vulcanisates

Storage modulus (G') of cured HNBR vulcanisates with various carbon black loadings is illustrated in Figure 4. Similar to uncured compounds without filler, unfilled vulcanisates reveals broader LVE region with insignificant magnitude of strain-dependent behaviour. By contrast, filled vulcanisates show significant strain-dependent modulus which is more pronounced in highly filled vulcanisates. Such insignificant magnitude of strain dependency is caused by the presence of chemical crosslink acting as spring component with elastic contribution. Additionally, the formation of rubber network via chemical crosslink leads to a rise in elastic modulus compared with the uncured compounds at a given carbon black loading.

Results of the damping factor (tanδ) as a function of shear strain in filled HNBR vulcanisates are depicted in Figure 5. By contrast to the uncured compounds, the filled vulcanisates exhibit an increase the in damping factor with carbon black loading, especially in highly filled vulcanisates. The increased damping factor can be attributed to the molecular slippage at interfaces between rubber and carbon black particles. It is known that the rubber-carbon black interaction is dominated by the physical over chemical interactions [34], unlike rubber-silane treated silica interaction. Thus, such relatively weak interactions would allow molecular flow at rubber-carbon black interfaces, and thus the rise in dissipated energy dissipation supports the hysteretic process. The higher the carbon black loading, the higher the positions available for hysteretic processes. Also, the swing-up of the damping behavior at high strain could be explained by the disruption of the carbon black transient network [32, 33]. From the overall results, it could be summarised that the damping behaviour of carbon black filled rubber compounds and vulcanisates is governed mainly by dilution effect and interfacial molecular flow, respectively.

Effect of carbon black specific surface area (particle size) Uncured HNBR compounds

In this part, the carbon black loading in compounds was kept constant at 60 phr in order to monitor the effects of the surface specific area on dynamic mechanical properties of uncured HNBR compounds. Figure 6



8 **Complex viscosity (η*) of uncured HNBR compounds as a function of carbon black specific surface area (measured at 1 rad/s, 10 % strain and 100 °C)**

shows G' as a function of the strain amplitude. It is evident that the strain-dependency of G' takes place in all uncured compounds with the greater magnitude found in compounds filled with carbon black having higher specific surface area. Also, at low strain amplitude, the magnitude of G' rise is more pronounced in HNBR filled with higher specific surface area (or smaller particle size) carbon black. This can be attributed mainly to the greater possibility for a formation of the filler network and the lower percolation threshold of the particles. [32].

Figure **7** illustrates results of tanδ in HNBR compounds which appear to decrease with increasing carbon black specific surface area, indicating an increase in elastic contribution. Referring to the discussion of G', the tridimensional transient filler network of carbon black which is more profound in carbon black with higher specific surface area is believed to be responsible for a rise in elastic behaviour.

Complex viscosity (η*) results as indication of processability in uncured compounds with carbon black having different specific surface areas (or particle sizes) at 100 °C are shown in Figure **8**. Expectedly, the specific surface area of carbon black plays profound effect on processability of uncured HNBR compounds, i.e., η* increases with increasing specific surface area of carbon black (N326 > N550 > N774 > N990). As discussed previously, the combination of hydrodynamic effect, rubber-filler and filler-filler interactions is responsible for molecular restriction, and so an increase in bulk viscosity. The carbon black with high specific surface area (i.e., small particle size) would possess greater contacting area between rubber and carbon black, and between carbon black aggregates, leading to a decrease in molecular mobility.

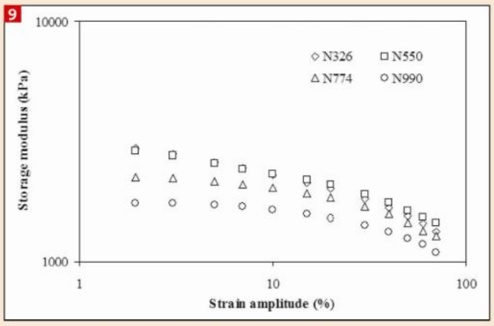
Cured HNBR vulcanisates

In the case of cured HNBR filled with 60 phr carbon black having various specific surface areas, results of G' as a function of deformation strain are shown in Figure **9**. The magnitude of G' rise appears to increase with increasing carbon black specific surface area, which could be explained by the greater contacting positions available for interaction between rubber and carbon black as well as between filler particles (or tridimensional transient filler network). It must be noted that, although N550 carbon black possesses smaller specific surface area than N326 carbon black, the vulcanisate with N550 shows comparable G' to that with N326. This is probably because of the high structure and crosslink density given by N550, as illustrated previously in Tables 1 and 3. Also, this phenomenon is not observed in uncured compounds, implying that such unexpected result of high G" found in specimen filled N550 must be a vulcanisation-related phenomenon.

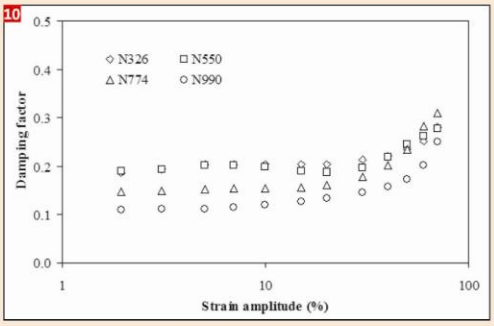
Figure **10** shows results of tanδ of filled HNBR vulcanisates. Clearly, tanδ increases with increasing carbon black specific surface area that means the higher energy dissipation through molecular flow at carbon black surfaces, as discussed previously in carbon black loading effect.

Mechanical properties

Mechanical properties of HNBR vulcanisates as function of carbon black loading and specific surface area are shown in Table **4**. It becomes evident that the tension values at 100 % elongation (M100) of cured HNBR increases with increasing carbon black loading and/or specific surface area. There are two main factors controlling the modulus M100, namely, the crosslink density of the rubber and the effect of filler reinforcement. According to Table 3, the degree of crosslink density apparently increases with carbon black loading, and the increased crosslink density would then yield the greater resistance to deformation via covalent bonds between rubber chains. Based on the results of the viscoelastic be-



9 **Storage modulus (G') as a function of strain amplitude of cured HNBR specimens (vulcanisates) with various carbon black specific surface area (measured at 1 rad/s and 60 °C)**



10 **Damping factor (tanδ) as a function of strain amplitude of cured HNBR specimens (vulcanisates) with various carbon black specific surface area (measured at 1 rad/s and 60 °C)**

havior (Fig. 5 and 10), the increase in damping factor as a function of both, the carbon black loading and the specific surface area is in good agreement with the increase in the M100 values of the corresponding vulcanisates. The increased carbon black loading and specific surface area mean a rise in contacting positions available for interactions between rubber molecules and the surface of carbon black. Also, the obstruction of rubber molecules by solid filler particlea or the hydrodynamic reinforcement could be another part of reason for an enhancement in the M100 values. Notably, the M100 values of vulcanisate with CB N550 appears to be close to that of CB N326 and becomes greater at high carbon black loading (60 phr) despite the relatively small specific surface area of CB N550. The results trend is similar to the one observed for Gc results discussed earlier. Thus, it is proposed that the reinforcement provided by N550 is governed by the crosslink density enhancement rather than the rubber-filler interaction.

The values obtained for tensile strength of filled HNBR vulcanisates are shown in Table 4. It is evident that strength of HNBR vulcanisates increases with increasing carbon black loading, which could be explained by filler reinforcement and/or crosslink density effects. Furthermore, it can be seen that tensile strength of HNBR filled with high specific surface area blacks is superior to the ones observed for small specific surface area blacks. Evidently, this is caused by filler reinforcement, as mentioned previously. However, an excessive crosslink density found particularly in vulcanisate with CB N550 might restrict molecular mobility, and thus a reduction in energy dissipation during being strained. This would end up with a decrease in mechanical strength [35]. One might notice that the strength of vulcanisate with CB N774 at high loading (60 phr) is highest among vulcanisates with CBN326, CB N550 and CB N990. The lowest strength found in CB N990 is not surprising as this black possesses relatively small specific surface area and low structure (low DBPA value) and thus low rubber-filler interaction. The apparently low strength observed in CB N326 at high loading is probably attributed to its relatively poor dispersion in HNBR. It is known that the capability of carbon black incorporation, distribution and dispersion is reduced with increasing specific surface area of the filler. Thus, some of undispersed CB N326 agglomerates might act as flaws in specimens leading to a reduction in tensile strength. In the case of CB N550, the excessive crosslink density might be responsible for a relatively low mechanical strength. Results of elongation at break (%EB) as illustrated in Table 4 agree well with the tensile strength result. From these results it holds: the greater the reinforcement, the lower the %EB. High extent of crosslink density and rubber-filler interaction would restrict molecular deformation and thus leading to a decrease in %EB.

In the case of carbon black loading and specific surface area effects on hardness of HNBR vulcanisates, it is apparent that the hardness increases with increasing carbon black loading. It is acknowledged that the relative deformation taking place in hardness test is relatively small. Consequently, the transient filler network in highly filled vulcanisates (i.e., HNBR vulcanisates with 60 phr N326 carbon black) might still influence the modulus at low strain (or hardness), and its effect is comparable to the crosslink density effect found in vulcanisates with CB N550.

The abrasion resistance of HNBR vulcanisates filled with various carbon black loadings is expressed as abrasion volume loss. It appears from Table 4 that, at a given specific surface area of carbon black, abrasion resistance is not significantly affected by carbon black loading. By contrast, at high carbon black loadings of 40 and 60 phr, both vulcanisates with N326 and N990 carbon black exhibit relatively low abrasion resistance. This phenomenon is probably due to poor filler dispersion at high loading of CB N326 having large specific surface area, and due to low magnitude of rubber-filler interaction of CB N990 possessing relatively low structure and specific surface area.

Conclusions

HNBR compounds and vulcanisates with various carbon black loadings and specific surface areas (or particle size) were prepared, and their cure, viscoelastic and mechanical properties were measured. Results obtained exhibit a significant dependence of cure behaviour (i.e., scorch time, optimum cure time and crosslink density) on carbon black loading and specific surface area. This dependence is explained in terms of thermal history, surface chemistry and thermal conductivity as a function of carbon black loading and specific surface area. Storage modulus and damping factor significantly increase with increasing carbon black specific surface area and loading of the blacks. The combined effect of hydrodynamic effect, filler transient network, molecular slippage at carbon black interfaces and crosslink density are proposed to be responsible for the viscoelastic properties. Mechanical properties are found to be governed by such combined effect associated probably with incomplete carbon black dispersion at high loading of carbon black (particularly in the case of relatively large specific surface area of carbon black, i.e., CB N326. The overall results imply a close correlation of viscoelastic and mechanical properties via energy dissipation process caused by molecular slippage at carbon black surfaces.

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5.2 กิจกรรมอื่นที่เกี่ยวข้องกับการนำผลจากโครงการไปใช้ประโยชน์

ทดลองนำเอาองค์ความรู้นี้ไปใช้กับสูตรยางคอมพาวด์ของผลิตภัณฑ์อื่นของทางบริษัท เช่น ลูกกลิ้งสำหรับอุตสาหกรรมเหล็กในตำแหน่งลูกกลิ้งที่ต้องทนต่อความร้อนและสารเคมี

5.3 ตารางเปรียบเทียบวัตถุประสงค์ กิจกรรมที่วางแผนไว้และกิจกรรมที่ดำเนินการมาและผลที่ได้รับตลอดโครงการ

กิจกรรมที่วางแผนไว้	**ผลที่ได้รับตลอดโครงการ**
- สามารถเตรียมยางผลิตภัณฑ์ HNBR ที่มีชนิดและปริมาณสารตัวเติมเสริมแรงต่างกันและศึกษาผลของชนิดและปริมาณสารตัวเติมต่อสมบัติด้านต่างๆ ของยางผลิตภัณฑ์	สามารถเตรียมยางผลิตภัณฑ์ HNBR ที่เติมสารตัวเติมต่างชนิดในปริมาณต่างกันทั้งระบบเขม่าดำ (ระบบเดี่ยวและระบบผสม) ระบบซิลิกา และระบบดินขาวอนุภาคนาโน โดยแต่ละระบบให้ปริมาณการเสริมแรงและสมบัติเชิงพลวัตที่ต่างกันชัดเจน
- สามารถปรับปรุงสมบัติด้านกระบวนการผลิต (Processability) โดยยังคงสมบัติเชิงกลที่ดี	สามารถปรับปรุงสมบัติด้านกระบวนการผลิตของยางผลิตภัณฑ์ HNBR โดยใช้สาร 3 ชนิด ได้แก่ ZDA TOTM และ TRIM โดยสารกลุ่ม TRIM มีความเหมาะสมมากที่สุดสำหรับงานนี้ เนื่องจากให้ Processability ที่ดีโดยไม่มีการสูญเสียสมบัติเชิงกล
- สามารถทำการ Scale-up เพื่อผลิตผลิตภัณฑ์ยาง	การได้สูตรยางคอมพาวด์ที่เหมาะสมการผลิต

ลูกกลิ้งขนาดใหญ่ โดยอาศัยข้อมูลที่ได้จากการทดลองเบื้องต้น	ผลิตภัณฑ์ยางลูกกลิ้งที่ใช้งานในอุตสาหกรรมกระดาษ และกำลังทดลองนำเอาองค์ความรู้นี้ไปใช้กับสูตรยางคอมพาวด์ของผลิตภัณฑ์อื่นของทางบริษัทที่ต้องการเน้นการความแข็งแรงเชิงกล ทนต่อความร้อนและน้ำมัน

5.4 ปัญหาและอุปสรรค

ปัญหาหลักของโครงการนี้อยู่ที่การ Scale up นำสูตรไปใช้ผลิตผลิตภัณฑ์ใช้งานจริง เนื่องจากการผลิตยางลูกกลิ้งจากยาง HNBR นี้ต้องรอคำสั่งผลิตจากลูกค้าของทางบริษัทลูกกลิ้งอุตสาหกรรมไทยจำกัด (ภาคเอกชนผู้ร่วมทุน) เพราะต้องทำการหุ้มยาง (Wrapping) ลงบนแกนเหล็ก (Metal cores) ที่ลูกค้าจัดส่งมาให้ทางบริษัทฯ ทำให้ต้องใช้เวลารอลูกค้าอยู่ระยะหนึ่ง สิ่งที่สำคัญคือลูกค้ากลุ่มดังกล่าวต้องเป็นลูกค้ากลุ่มที่สามารถทำความเข้าใจเกี่ยวกับงานด้าน R&D ที่ต้องมีการยินยอมให้มีการทดลองใช้งานและปรับแต่งในเรื่องต่างๆ ซึ่งอาจกระทบต่องานของลูกค้าบ้าง ซึ่งลูกค้ากลุ่มนี้มักเป็นบริษัทที่ใหญ่มีงานผลิตแน่น ทำให้มี Downtime ไม่นานนักส่งผลให้ทางบริษัทฯต้องรอช่วงเวลาเข้าทดสอบใช้งานที่ Site งานของลูกค้าดังกล่าวทำให้เกิดความล่าช้าต่อการปิดโครงการวิจัยนี้

ปัญหาหลักอีกประการคือเรื่องของการตีพิมพ์ผลงานวิจัย โดยมีปัญหาของ Conflict of interest กล่าวคือทางกรรมการพิจารณาบทความของวารสาร (Journal reviewer) ต้องการให้เปิดเผยรายละเอียดของสารเคมีที่ใช้ทั้งหมด แต่ทางบริษัทไม่ยินยอมเนื่องมาจากกำลังใช้งานองค์ความรู้นี้ในการผลิตผลิตภัณฑ์เพื่อการค้าอยู่ ซึ่งการเปิดเผยอาจส่งผลเสียต่อผลประโยชน์ของทางบริษัท ดังนั้น

คณะผู้วิจัยจึงต้องพยายามเรียบเรียงเนื้อหาบทความที่จะตีพิมพ์ในลักษณะที่ต้องประณีประณอม เช่น การตัดผลของบางตัวแปรออกจากบทความและหาข้อมูลส่วนอื่นมาแทนที่ ทำให้ใช้เวลาในการตีพิมพ์นานมากกว่าปรกติ อย่างไรก็ตามคาดว่าเมื่อทุกอย่างลงตัวน่าจะสามารถตีพิมพ์ผลงานในวารสารวิชาการได้อย่างน้อย 2 เรื่อง