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5. ภาคผนวก

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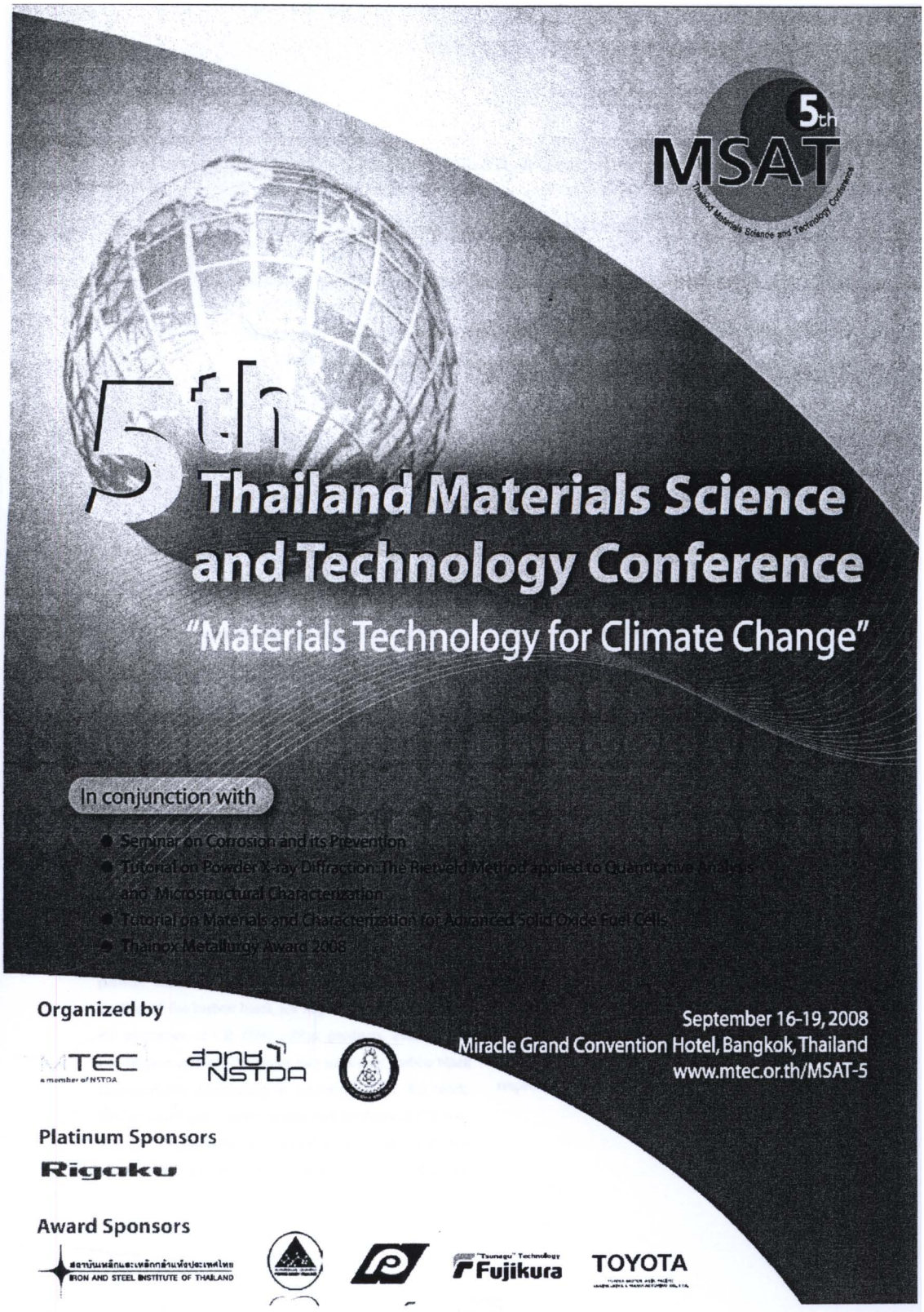
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Viscoelastic behaviour of Carbon Black-Filled Hydrogenated acrylonitrile butadiene rubber

Panjaporn Wongwitthayakool[1], Chakrit Sirisinha[2]

[1] Department of Chemistry, Faculty of Science, Mahidol University, Bangkok 10400
Phone 0-2441-9816, Fax.0-2441-0511, E-Mail: g5038025@student.mahidol.ac.th

[2] Department of Chemistry, Faculty of Science, Mahidol University, Bangkok 10400
Phone 0-2441-9816, Fax.0-2441-0511, E-Mail: scesr@mahidol.ac.th

Abstract

Various grades and loading of carbon black (CB) as reinforcing filler was incorporated into hydrogenated acrylonitrile butadiene rubber (HNBR). Viscoelastic behaviour of HNBR compounds and vulcanisates was investigated using the Rubber Process Analyser (RPA2000). Results obtained reveal increases in storage modulus (G′), damping factor (tanδ) and complex viscosity (η*) with increasing loading and surface area of CB, and the reinforcement mechanism is discussed.

1. Introduction

Hydrogenated acrylonitrile butadiene rubber (HNBR) is wide adopted in automotive, industrial, and assorted, performance-demanding applications due its excellent thermal stability, high chemical resistance, very good mechanical strength with high elasticity [1-2]. As fillers are incorporated into rubber, apart from positive change in mechanical properties, the change in viscoelastic behaviour is observed [3-10]. Carbon black (CB) is the most popular filler used in rubber industries as reinforcing filler. Its particle size, structure, surface chemical structure, and loading of the carbon black are important factors affecting the properties of CB filled rubber products. Particle size and surface area are the major two important carbon black characteristics determining its performance. In this work, HNBR filled with various grades and loadings of CB (i.e., N326, N774 and N990) were prepared to investigate effects of particle size and surface area of carbon black on viscoelastic behaviour of HNBR compounds and vulcanisates.

2. Experimental

2.1 Materials

HNBR with acrylonitrile content and Mooney viscosity (ML(1+4) 100°C) of 34% and 55, respectively, was provided by Lanxess Co., Ltd. Four different grades and loading of carbon black were used, i.e., N326, N774 and N990. Other compounding ingredients included zinc oxide (5 phr), stearic acid (1 phr), TMQ (1 phr), TOTM (5 phr) and DCP (2 phr). All chemicals were used as-received.

2.2 Samples Preparation

Samples of HNBR filled with different CB loadings from 0 to 60 phr were prepared using a lab-scale open mill (LabTech, Thailand) at set temperature of 40°C. In the initial step of mixing, HNBR was masticated and then CB and other compounding ingredients were charged sequentially. The total mixing time used was 20 minutes.

2.2 Measurement of cure characteristics

Cure characteristics were measured 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.

2.3 Measurement of viscoelastic behaviour

Viscoelastic behaviour of HNBR compounds were measured using the RPA2000 at a test temperature of 100°C.

3. Results and Discussion

3.1 Cure Characteristics

Table 1 illustrates cure behaviour, i.e., scorch time (t_{s2}), cure time (t_{c90} and t_{c99}) and torque difference between the maximum and minimum torques ($\Delta S'$) as an indicator for crosslink density. It can be seen that both changes in CB loading and particle size do not gives much influence on t_{s2}, t_{c90} and t_{c99} of HNBR compounds. However, the crosslink density appears to increase with the increases in CB loading which is attributed to the increases in thermal conductivity and/or surface activity of compounds as provided by CB.

Table 1 Curing characteristics of HNBR and filled HNBR

CB grade	Loading (phr)	t_{s2} (min)	t_{c90} (min)	t_{c99} (min)	$\Delta S'$ (dNm)
N326	0	1.41	74.00	112.54	28.33
	10	1.32	75.03	113.11	31.98
	20	1.16	73.96	112.38	36.39
	40	1.06	71.88	111.67	42.74
	60	0.95	69.12	110.42	49.00
N774	10	1.34	74.15	112.43	34.46
	20	1.21	72.94	111.36	38.47
	40	1.03	72.93	112.15	45.08
	60	0.96	71.79	111.49	48.74
N990	10	1.30	75.16	113.02	33.31
	20	1.24	76.01	113.16	35.69
	40	1.14	75.50	112.26	41.58
	60	1.07	75.76	112.91	46.31

3.2 Viscoelastic properties

Storage modulus (G') of cured HNBR with various carbon black loadings is shown in Figure 1. It is evident that G' increases with increasing CB loading, which is attributed to the reinforcing effect, i.e. hydrodynamic effect, filler-filler interaction, as well as, filler-rubber interaction. The highly filled elastomers are known to show the strong filler transient network (or "Payne effect"), leading to a remarkable rise in G' at low strain of deformation and a drop in G' at high strain [11]. Also, it can be seen that the magnitude of increase in G' is greater in HNBR filled with smaller particle size of CB which is due mainly to the greater possibility for tridimensional transient network formation of CB via its higher surface area.

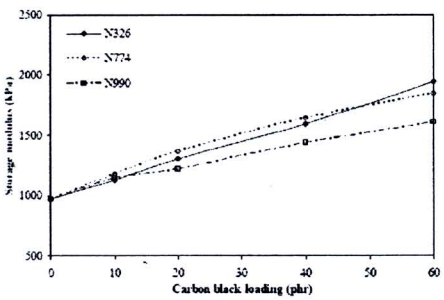

Figure 1 Relationship between storage modulus and carbon black loading of cured HNBR with different carbon black loadings (10% strain, 1 rad/s and 100°C)

Figure 2 exhibits results of damping factor (tanδ) at 10% strain as a function of CB loading in HNBR filled with various CB grades. Clearly, tanδ of all HNBR vulcanisates increases with increasing CB loading, particularly in the case of CB with high surface area (or small particle size). The greater surface area leads to the greater contact positions available for rubber molecules and thus the higher energy dissipation [11].

Processability of HNBR compounds is monitored in terms of complex viscosity (η^*), as shown in Figure 3. As expected, the η^* of all compounds increases with

increasing loading and surface area of CB. The increase in η* with increasing CB loading and surface area is in good agreement with the reinforcing effect, as discussed previously. In other words, the processability appears to decrease due to the flow obstruction by: solid particle of CB (hydrodynamic effect) (i), HNBR-CB interaction (ii), tridimensional transient network of CB (iii).

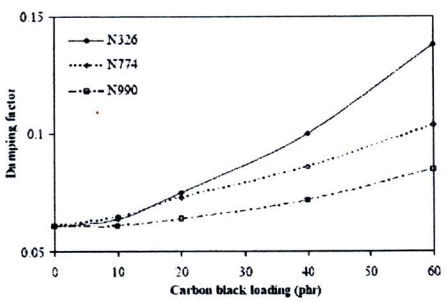

Figure 2 Relationship between damping factor (tanδ) and carbon black loading of cured HNBR with different carbon black loadings (10% strain, 1 rad/s and 100°C)

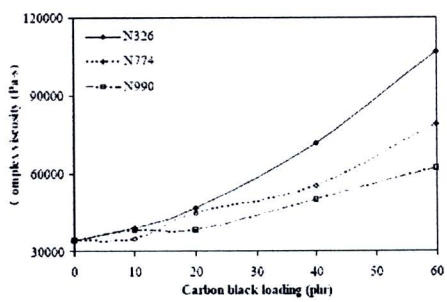

Figure 3 Relationship between complex viscosity and carbon black loading of uncured HNBR with different carbon black loadings (10% strain, 1 rad/s and 100°C)

4. Conclusions

Viscoelastic behaviour of HNBR filled with various loadings and grades of carbon black was investigated in this work. Results obtained show that, by varying CB loading, cure behaviour is not significantly affected. As surface area of CB increases, a rise in crosslink density is observed. In terms of viscoelastic behaviour, it is found that increases in CB loading and surface area cause a rise in reinforcing effect as determined from storage modulus and damping factor. The smaller the CB particle size, the greater the magnitude of the Payne effect. Also, a profound effect of increased CB loading and surface area on processability of HNBR compounds is observed.

Acknowledgment

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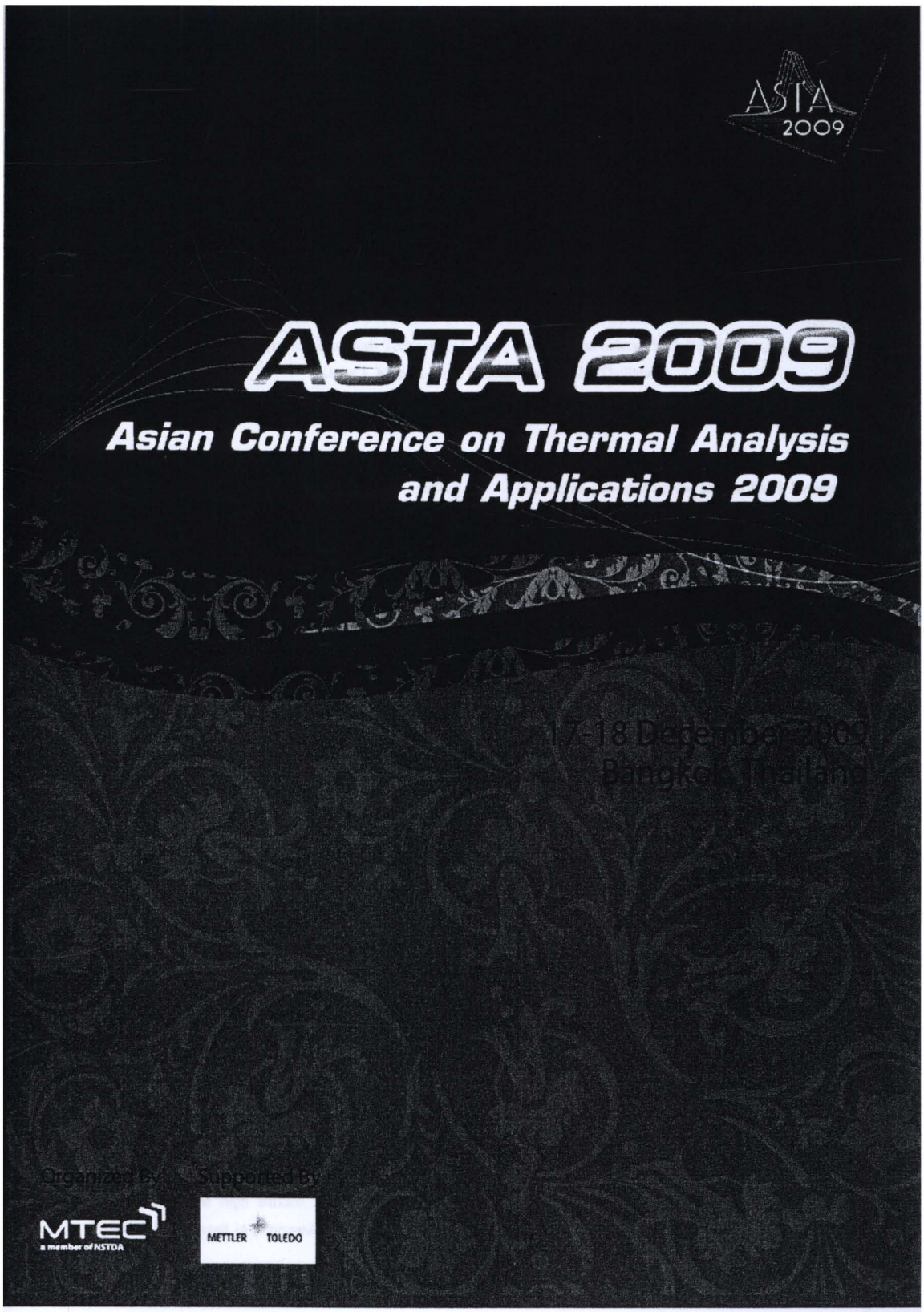
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Effect of Carbon black Hybrid System on Cure Behaviour and Dynamic Mechanical Properties of Hydrogenated Acrylonitrile Butadiene Rubber

Panjaporn Wongwitthavakool[1], Chakrit Sirisinha[2] and Pongdhorn Saeolu[3]

[1] Department of Chemistry, Faculty of Science, Mahidol University, Bangkok 10400

Phone 0-2441-9816, Fax.0-2441-0511, E-Mail: g5038025@student.mahidol.ac.th

[2] Department of Chemistry, Faculty of Science, Mahidol University, Bangkok 10400

Phone 0-2441-9816, Fax.0-2441-0511, E-Mail: sccsr@mahidol.ac.th

[3] National Metal and Materials Technology Center, 114 Thailand Science Park Paholyothin Rd., Klong 1, Klong Luang, Pathumthani 12120, Thailand.

Abstract

Hydrogenated acrylonitrile butadiene rubber (HNBR) was reinforced with carbon black hybrid as reinforcing fillers. Influence of N326 and N990 carbon black hybrid ratio on cure behaviour and dynamic mechanical properties was investigated. Dynamic mechanical behaviour of filled HNBR vulcanisates was investigated using the dynamic mechanical analyser (DMA). Results obtained reveal increases in storage modulus (G') and loss factor (tanδ) with increasing larger surface area and higher structure of carbon black, and the reinforcement mechanism is discussed.

1. Introduction

The reinforcement mechanism of filled rubber is believed to be caused by hydrodynamic effect and filler-filler together with rubber-filler interactions [1]. In general, the reinforcement magnitude could be characterised by mechanical as well as rheological properties [2-4].

Carbon black is the most popular filler used in rubber industries as reinforcing filler. Its particle size, structure, surface chemical structure, and loading of the carbon black are important factors affecting the properties of carbon black filled rubber products. Carbon black characteristics (i.e., specific surface area and structure) are known to influence reinforcement magnitude. The high surface area and structure of carbon black result in improved mechanical properties [5,6]. On the other hand, the strong rubber-filler interaction provided by the carbon black having high surface area and structure gives rise to an increase in compound viscosity, and thus poor processability [7].

Hydrogenated acrylonitrile butadiene rubber (HNBR) is a high-performance rubber specifically used in application where high resistances to hydrocarbon oil and thermal ageing are required. Consequently, HNBR is widely adopted in automotive, industrial, and assorted, performance-demanding applications [5,8]. Despites its high mechanical properties, further reinforcement with the uses of reinforcing fillers is still of interest in order to gain the HNBR vulcanisates with excellent mechanical properties and with reduced production cost in some circumstances.

In the present study, a carbon black hybrid system composing of N326 and N990 carbon blacks having different specific surface areas and structures was mixed with hydrogenated acrylonitrile butadiene rubber (HNBR). Cure behaviour and reinforcement magnitude were monitored and discussed. The dynamic mechanical properties determined from dynamic mechanical analyser (DMA) are applied for the study of the reinforcing effect.

2. Experimental

2.1 Materials

The compounding formulation used for preparing HNBR compounds and vulcanisates in this work is illustrated in Table 1.

Table 1 Compounding ingredients used in the present study

Material	Amount (phr)	Grade/Supplier	Function
HNBR	100	Therban® VP KA 8837 (34% acrylonitrile content, Mooney viscosity (ML1+4 at 100°C) = 55)/Lanxess Co., Ltd., Thailand	Rubber matrix
Carbon black	60[a]	N326, N550/Loxley Public Co., Ltd., Thailand N990/Saim Luck Trading Co., Ltd., Thailand	Reinforcing filler
TMQ[b]	1	Vulkanox HS/Bayer International S. A., Thailand	Antioxidant
TOTM[c]	5	TOTM (STAB)/Behn Meyer Chemical (Thailand) Co., Ltd.., Thailand	Plasticiser
DCP[d]	2	Percumyl D/Petchthai Chemical Co., Ltd., Thailand	Curing agent

[a] Carbon black hybrid ratio (N326/N990): 0/60, 12/48, 24/36, 36/24, 48/12 and 60/0

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

[c] Tri-2-ethylhexyl trimellitate

[d] Dicumyl peroxide

A carbon black hybrid system composing of N326 and N990 having different characteristics (i.e., surface area and structure) as shown in Table 2 [9] was utilised with the total carbon black content of 60 phr. Compared with N990, the N326 carbon black possesses higher surface area (smaller particle size) and structure as indicated by the values of iodine adsorption and DBP absorption, respectively.

Table 2 Carbon black properties

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

2.2 Samples Preparation

Mixing of HNBR with carbon was performed using a lab-scale open mill (LabTech Co., Ltd., Bangkok, Thailand) at set temperature of 40°C. In the initial step of mixing, HNBR was masticated and then carbon black and other compounding ingredients were charged sequentially. The total mixing time of 20 minutes was used throughout the whole work.

2.3 Characterisations

Cure characteristics

Cure characteristics of HNBR/carbon black hybrid system were measured 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}) and cure time (t_{c90}) were determined from the time to achieve torque rise of 2 units above the minimum torque, and the time to reach 90% complete cure state, respectively. Torque difference ($\Delta S'$), the difference between the maximum (S'_{max}) and minimum storage torque (S'_{min}), is considered as the indication of crosslink density [10].

Dynamic mechanical properties

The dynamic mechanical properties of HNBR vulcanisates were measured using a dynamic

mechanical analyser (Gabo, Explexor™ 25N) in a tension mode. Two types of tests, namely, temperature sweep (-80 to +120°C) and strain sweep (0.1 to 10 %strain amplitude) tests were performed.

3. Results and Discussion

3.1 Cure Characteristics

Table 3 reveals cure behaviour, i.e., scorch time (t_{s2}), cure time (t_{c90}) and torque difference ($\Delta S'$) as a measure of crosslink density of HNBR filled with carbon black hybrid system. Apparently, there is no significant change scorch time (t_{s2}). Cure time (t_{c90}) slightly decreases while torque difference increases with increasing N326 content. These results indicate a *cure promotion phenomenon* provided by the rise in surface area and structure of carbon black into carbon black hybrid system, which is probably due to the thermal history effect. As the content of N326 possessing relatively high surface area and structure increases, the increase in filler-polymer interaction leads to increased bulk viscosity via viscous dissipation. The increased thermal energy applied to the bulk during mixing gives the shortened time required for curative dissociation and so the cure promotion phenomenon.

Table 3 Curing characteristics of filled HNBR with carbon black hybrid system

N326/N990 Ratios	t_{s2} (min)	t_{c90} (min)	$\Delta S'$ (dNm)
0/60	1.09±0.09	70.84±1.13	53.40±2.58
12/48	1.06±0.04	70.53±0.78	54.12±2.35
24/36	1.02±0.04	68.96±1.35	53.74±2.74
36/24	1.02±0.00	66.28±1.81	56.48±3.61
48/12	1.00±0.01	66.22±1.49	59.32±1.14
60/0	1.01±0.04	62.62±2.50	60.19±0.04

3.2 Dynamic Mechanical properties

Strain sweep test

Storage modulus (G') of HNBR vulcanisates filled with carbon black hybrid system as a function of strain amplitude is shown in **Figure 1**. It is evident that G' increases with increasing N326 content, which is attributed to the reinforcing effect, i.e. hydrodynamic effect, filler-filler interaction, as well as, filler-rubber interaction. The presence of N326 with relatively high surface area and structure is reported to yield the strong filler transient network (or "*Payne effect*"), leading to a remarkable rise in G' particularly at low strain of deformation. At high strain, the G' decreases as a result of filler transient network disruption [11].

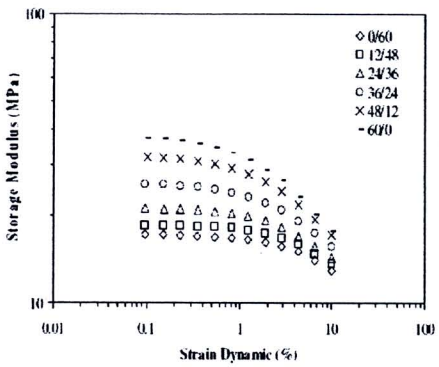

Figure 1 Storage modulus (G') as a function of strain amplitude of cured HNBR specimens (vulcanisates) with various N326/N990 ratios at test temperature of 60°C

To simplify the G' results, the values of G' as a function of N326/N990 ratios at a given strain of 0.1% is plotted, as shown in **Figure 2**. Obviously, the increase in G' with increasing N326 content of HNBR vulcanisates is in good accordance with the rule of mixtures [12] as shown in Equation 1.

$$G' = G_1' W_1 + G_2' W_2 \qquad (1)$$

where

G': Storage modulus of filled HNBR with carbon black hybrid system

G_1': Storage modulus of filled HNBR with N326

G_2': Storage modulus of filled HNBR with N990

W_1: Weight fraction of N326 filled in HNBR

W_2 : Weight fraction of N990 filled in HNBR

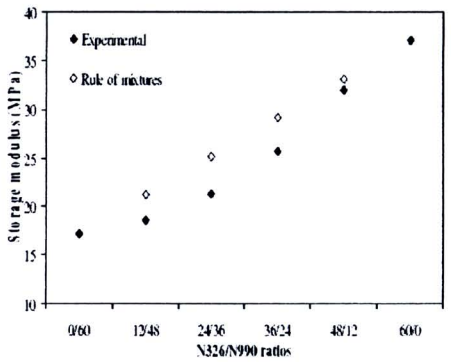

Figure 2 Storage modulus (G') of cured HNBR specimens (vulcanisates) calculated from the rule of mixtures equation and experimental results as a function of various N326/N990 ratios at test temperature of 60°C

Figure 3 exhibits results of loss factor or damping factor (tanδ) as a function of strain amplitude of carbon black filled HNBR. Clearly, tanδ of all HNBR vulcanisates increases with increasing N326 in hybrid system, which is more noticeable at the strain beyond 0.1 %strain. The relatively high surface area and structure leads to the greater contacting positions available for rubber molecules and thus the higher energy dissipation [10].

Temperature sweep test

Figure 4 demonstrates G' of carbon black hybrid system filled HNBR. The values of T_g as determined from abrupt change in G' are not significantly affected by carbon black composition ratio in a hybrid system. As expected, the values of G' at temperature of 60°C agrees well with those determined from the strain sweep test, as revealed earlier in **Figure 1**. The vulcanisates with greater content of N326 exhibit higher magnitude of reinforcement.

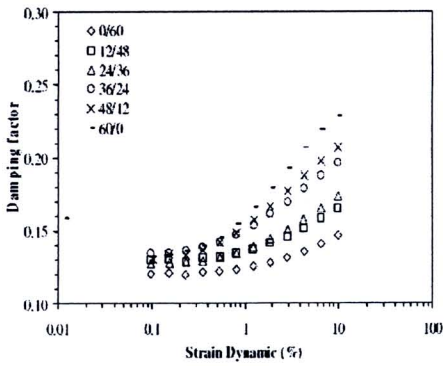

Figure 3 Damping factor (tanδ) as a function of strain amplitude of cured HNBR specimens (vulcanisates) with various N326/N990 ratios at test temperature of 60°C

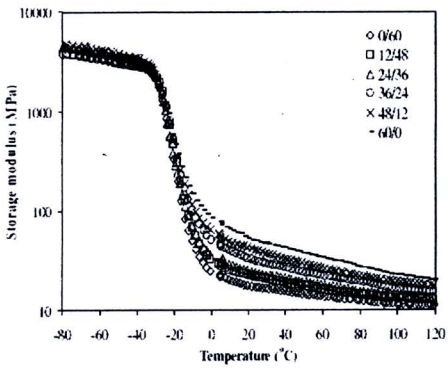

Figure 4 Storage modulus (G') as a function of temperature of cured HNBR specimens (vulcanisates) with various N326/N990 ratios

Damping factor (tanδ) over a temperature range of -80 to 120°C is given in **Figure 5**. Clearly, the damping peaks of filled HNBR decrease with the increasing N326 content, implying the restricted molecular mobility (or HNBR segmental motions) via the increased rubber-carbon black interaction. On the contrary, the damping factor in the rubbery plateau appears to increase with increasing N326 content, which is consistent with the results measured from the

strain sweep test as shown previously in **Figure 3**. The higher damping factor at rubbery plateau would cause the higher extent of heat build-up found in tyre and industrial roll applications.

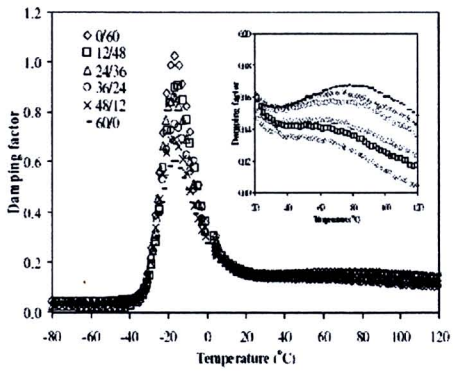

Figure 5 Damping factor (tanδ) as a function of temperature of cured HNBR specimens (vulcanisates) with various N326/N990 ratios

4. Conclusions

A peroxide cured HNBR vulcanisates reinforced by the N326/N990 hybrid system was prepared. Cure behaviour and dynamic mechanical properties were investigated. Results obtained show that, as loading of N326 in hybrid system increases, a rise in crosslink density (as determined from the cure torque difference) is observed. Not only crosslink density but also reinforcement is controlled strongly by N326 with relatively high surface area and structure rather than the N990. The magnitude of reinforcement appears to be in line with the rule of mixtures. The increases in surface area and structure of carbon black reveal the increased extents of Payne effect and molecular mobility restriction.

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Plastics, Rubber and Composites: Macromolecular Engineering

Subject: Your submission PRCME2861
From: "Plastics, Rubber and Composites" <xwang5@bradford.ac.uk>
Date: 4 Oct 2010 11:56:39 -0400
To: "Chakrit Sirisinha" <cs018072742@yahoo.com>

Ref.: PRCME2861
A PREDICTION OF HEAT BUILD-UP BEHAVIOUR UNDER HIGH-LOAD BY THE USE OF CONVENTIONAL VISCOELASTIC RESULTS IN CARBON BLACK-FILLED HYDROGENATED NITRILE RUBBER
Plastics, Rubber and Composites: Macromolecular Engineering

Dear Dr. Sirisinha

We have now received reviewers' comments on the above submission. I am pleased to tell you that the work is found to be of interest and is likely to be suitable for publication in Plastics, Rubber and Composites: Macromolecular Engineering, subject to your consideration of some points which have been raised. These are detailed in the comments below.

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When resubmitting, please provide a list of changes and, where appropriate, respond to each point which has been raised. You should upload this response as a separate file during the resubmission process. Please ensure that you supply a text file prepared according to the specification in the instructions to authors (SEE IMPORTANT NOTE ON EQUATIONS BELOW) and a high resolution image file of each figure. Failure to do this may result in a delay in the typesetting of your paper. Please note that it is not permitted to submit a PDF file of the revised manuscript at this stage.

Thank you for submitting your work to this journal.

With kind regards

James Busfield, PhD CEng FIMMM FHEA MA
Associate Editor
Plastics, Rubber and Composites: Macromolecular Engineering

Comments from the Editors and Reviewers:

Reviewer #1:

This is an interesting paper that merits publication. I would suggest that the authors should state the precise RPA 2000 test conditions (frequency, shape of the sample). I would also like the authors to justify why the viscoelastic and HBU properties are measured with two different temperatures (60°C and 100°C + HBU).

Reviewer #2:

This paper should be published subject o the following mandatory minor modifications.

Authors should mention occluded rubber as a factor of reinforcement especially for carbon black with high DBP. This might explain the ranking of N550 compare to N326 (Fig. 4 and 5) rather than cross-linking density. Also, Fig. 4 could be plotted using G'/G' at 80 Hz. This will allow enhancing the ranking of the 4 carbon blacks focusing on strain amplitude effect only.

The "3 dimensional transient network of CB" should be name percolated CB network. CB phr percolation threshold should be evaluated (e.g. electrical conductivity) to give a more precise status on CB phr influence on viscoelastic properties. This threshold is commonly comprise between 20 and 40 phr. With that information, conclusions of

Fig. 1, 2 and 3 may be enhanced.

Payne effect can also be explained by the evolution of the thickness of the glassy polymer layer around CB with stress amplitude.

Authors should give a clear status about the testing condition chosen for G'' and tan(d) (Fig. 9 and 10) and demonstrate that changing the chosen conditions (amplitude, frequency) does not influence the conclusion about the ranking of the R^2 factors.

The authors should explain why correlation between those 2 measures is still possible even if the measurement temperatures are different.

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Manuscripts containing equations must be produced in Word 2007 compatibility mode using Equation Editor 3.0 or in an earlier version of Word. Equations generated by Word 2007 are stored as images and cannot be used for typesetting. See http://www.maney.co.uk/instructions_for_authors/prc/ for further details.

A PREDICTION OF HEAT BUILD-UP BEHAVIOUR UNDER HIGH-LOAD BY THE USE OF CONVENTIONAL VISCOELASTIC RESULTS IN CARBON BLACK-FILLED HYDROGENATED NITRILE RUBBER

Panjaporn WONGWITTHAYAKOOL[a], Pongdhorn SAEOUI[b] and Chakrit SIRISINHA*[a,c]

[a] **Department of Chemistry, Faculty of Science, Mahidol University, Rama 6 Rd., Bangkok 10400, Thailand.**

[b] **National Metal and Materials Technology Center, 114 Thailand Science Park Paholyothin Rd., Klong 1, Klong Luang, Pathumthani 12120, Thailand.**

[c] **Research and Development Centre for Thai Rubber Industry (RDCTRI), Faculty of Science, Mahidol University, Salaya Campus, Phutthamonthon 4 Rd., Salaya , Nakhon Pathom, 73170, Thailand.**

* To whom correspondence should be addressed

FAX: +662-441-0511; e-mail: sccsr@mahidol.ac.th

ABSTRACT

Viscoelastic and heat-build up (HBU) properties of HNBR filled with various loadings and characteristics of carbon black (CB) were determined using RPA2000 and Gabometer4000 flexometer equipped with high load cell, respectively. A correlation of viscoelastic results measured routinely to the HBU results is drawn. Reinforcement mechanism is proposed as interplay of hydrodynamic effect, filler transient network, molecular slippage and crosslink density. Also, the HBU significantly increases with increasing CB loading and/or surface area, which is probably the result of hysteretic process. As a prediction of HBU under high load, the loss modulus is superior to the damping factor.

Key words: Reinforcement; Viscoelastic properties; Carbon black; Heat build-up; Hydrogenated nitrile rubber

1. INTRODUCTION

Hydrogenated acrylonitrile butadiene rubber (HNBR) is a high-performance rubber specifically used in application where high resistances to hydrocarbon oil and thermal ageing are required. Consequently, HNBR is widely adopted in automotive, industrial, and assorted, performance-demanding applications. Despites its high mechanical properties, further reinforcement with the uses of reinforcing fillers is still of interest in order to gain the HNBR vulcanisates having excellent mechanical properties and in conjunction with reduced production cost in some circumstances.

Carbon black is the most popular filler used in rubber industries as reinforcing filler. Particle size, structure, surface chemistry and loading of carbon black are known to be important factors affecting properties of carbon black filled rubber products. Carbon black characteristics (i.e., specific surface area and structure) have been reported to significantly influence the reinforcement magnitude, which could be determined from the viscoelastic properties, as expressed in terms of storage modulus (G'), loss modulus (G") and damping factor (tanδ). Numerous works [1-5] reveal that carbon black surface areas and loadings play strong roles in viscoelastic behaviour of filled rubber.

Basically, the reinforcement mechanism of carbon black filled rubber is believed to be caused by hydrodynamic effect and carbon black-carbon black together with rubber-carbon black interactions [6]. Although the presence of rubber-carbon black interaction leads to a high extent of reinforcement, such

interaction gives rise to the high magnitude of heat build-up (HBU) found in rubber products. This is because of the fact that the rubber-carbon black interaction is dominated by the physical over chemical interactions [7], allowing molecular flow at rubber-carbon black interfaces, and thus the greater energy dissipation via hysteretic process [8].

In carbon black filled rubber such as natural rubber (NR), the HBU increases with increasing hysteresis loss, implying a correlation of HBU to viscoelastic behaviour to some extent [9]. Consequently, the present study aims to investigate the interconnection between HBU and viscoelastic properties of HNBR filled with carbon blacks having different surface area and structure. Generally, HBU measurement is carried out using a conventional Goodrich flexometer under low static stress (0.99 MPa), which is not suitable for such high-modulus rubber vulcanisates as industrial roll products. The stress-controlled flexometer provided with high load force, i.e., the Gabometer 4000 in this case was therefore used. To measure the viscoelastic properties of HNBR vulcanisates as routine tests, the Rubber Process Analyser (RPA2000) was utillised. The prediction of HBU by the routine measurement of viscoelastic properties was conducted and discussed.

EXPERIMENTAL

2.1 Materials

Raw HNBR (Therban® VP KA 8837) having acrylonitrile and unsaturation contents of 34% and 18%, respectively was purchased from Lanxess Co., Ltd.

(Bangkok, Thailand). Four grades of carbon blacks (N326, N550, N774 and N990) with different characteristics (i.e., surface area and structure) supplied by Loxley Public Co., Ltd. (Bangkok, Thailand) and Siam Luck Trading Co., Ltd. (Bangkok, Thailand) were used as reinforcing filler. Referred to ASTM D 1765-00 [10], the specific surface area as specified by iodine absorption value and degree of structure as determined by DBP absorption test are shown in **Table 1**. The specific surface areas of carbon blacks used in this work are in the order as follows: N326 > N550 > N774 > N990 while degree of structure is in the following order: N550 > N326 ~ N774 > N990. The tri-2-ethylhexyl trimellitate (TOTM) as plasticiser was purchased from Behn Meyer Chemical (Thailand) Co., Ltd. (Bangkok, Thailand). Dicumyl peroxide (98% active) as a curing gent was supplied by Petchthai Chemical Co., Ltd (Bangkok, Thailand).

2.2 Samples Preparation

The formulation of HNBR compounds prepared is listed in **Table 2**. The mixing process was commenced on a lab-scale open mill (LabTech Co., Ltd., Bangkok, Thailand) at set temperature of 40°C. Then, the masticated HNBR was compounded with prepared carbon black and chemicals, as illustrated in **Table 2**, on the mill for 20 minutes. To prepare cylindrical in shape, having diameters of 17.8±0.1 mm and heights of 25±0.15 mm in accordance with ASTM-D-623-93 for the HBU measurement [10], the compounds prepared were compression moulded at 145°C under moulding pressure of 150 kg/cm^2 for 120 minutes.

2.3 Characterisations

Viscoelastic properties

Viscoelastic behaviour of HNBR vulcanisates were measured using the Rubber Process Analyser (RPA2000, Alpha Technologies, USA). Strain sweep test was conducted, and the resultant storage modulus or elastic modulus (G′), loss modulus or viscous modulus (G″) and damping factor or loss factor (tanδ) were recorded at 60°C. It must be noted that the time sweep test was initially performed to monitor thermal stability of test specimens, so that it could be ensured that any change in results of strain sweep tests is not caused mainly by a thermal degradation.

Heat-build up (HBU) behaviour

Gabometer 4000 was utillised to determine the magnitude of HBU in HNBR vulcanisates under high static stress of 1.97 MPa at test temperature, frequency and dynamic displacement of 100°C, 15 Hz and 2.2 mm, respectively. The test duration used was of 25 minutes.

3. RESULTS AND DISCUSSION

To investigate the viscoelastic properties of HNBR vulcanisates filled with different types and loadings of carbon black, the RPA2000 as the oscillatory rheometer specially designed for elastomer was used. The RPA2000 has gained interest from rubber technologists due to its ease of operation and

precise data measured. In general, the time, strain and frequency sweep tests are usually performed giving valuable data correlating to the rubber processing aspect. In the view of dynamic mechanical properties of vulcanisates particularly the heat-build-up (HBU) behaviour, the conventional Goodrich flexometer is usually utilised. However, in some industrial roll products in which high stress is applied to the rolls, the high modulus of rubber vulcanisates covering over the metal cores is required in order to prevent excessive deformation. This means the high modulus of roll products is needed. The precise prediction of HBU behaviour of this high-modulus rubber vulcanisates is not practical with the use of conventional Goodrich flexometer under the static stress of only 0.99 MPa. Consequently, the stress-controlled flexometer equipped with high load cell (up to 4,000 N), namely, Gabometer 4000, was used to measure the HBU of rubber vulcanisates in the present work. It is of our interest to establish correlation of HBU under high applied stress and viscoelastic results measured from RPA2000. By this means, if that correlation is a significant, it is possible to predict the HBU behaviours from the viscoelastic results measured from RPA2000 as routine test.

3.1 Viscoelastic properties

Effect of carbon black loading

Dynamic mechanical properties of cured HNBR with various carbon black loadings as determined from RPA2000 are shown in **Figs. 1, 2 and 3**. It is evident from **Fig. 1** that an unfilled compound possesses the lowest G′ and

broadest plateau of linear viscoelastic region (LVE) of up to 20% strain. Further increase in strain leads to the drop in G', due to the molecular flow of uncured portion existing in HNBR vulcanisates. Also, G' increases with increasing carbon black loading, which is due mainly to three main reasons as follows: flow field obstruction of rubber molecules by undeformable carbon black aggregates usually known as a *hydrodynamic effect* (i); flow restriction caused by a strong filler-rubber interaction at surfaces of carbon black aggregates (ii); and molecular flow reduction by the formation of three dimensional transient network of carbon black (iii) [4,8]. However, such transient network could be disrupted by high deformation yielding a strain-softening phenomenon at high strain or the so-called Payne effect [8]. The magnitude of is Payne effect appears to increase with increasing carbon black loading which is in line with previous work [4,11].

Fig. 2 reveals the results of loss modulus (G") in which G" of all compounds increases with increasing carbon black loading. This is because of the hydrodynamic effect, filler-rubber interaction as well as filler-filler interaction, as discussed in G' results. It is reported that the G" is dependent on rates of transient network breakdown and reformation under dynamic strain. The processes of filler network breakdown and reformation cause additional energy dissipation [8]. In HNBR vulcanisates filled carbon black loading up to 20 phr where the magnitude of filler transient network is relatively small (see **Fig. 1**), G" appears to be independent of strain up to 20% and then slightly increase with increasing shear strain, which could be caused by the viscous

dissipation via molecular flow. By contrast, with further carbon black loading, the HNBR vulcanisates initially reveal the reduction in G" with strain amplitude followed by the somewhat rise in G" at high strain. The reduction in G" is in good accordance with the fact that the transient filler network is destroyed and could not be reconstructed. At high strain of deformation where the filler transient network is already disrupted, the viscous dissipation via molecular flow at carbon black surfaces is believed to be responsible for the slight increase in G".

Fig. 3 demonstrates the change in damping factor or tanδ, which is the ratio of loss to storage moduli, as a function of deformation strain. In general, the damping factor could be used to imply the magnitude of viscous response per unit of elastic response. It is evident that the damping factor of all vulcanisates increases with increasing strain amplitude, indicating the rise in magnitude of viscous contribution dominating over the elastic one. The increase in damping factor is reported to be the result of energy dissipation through a molecular slippage associated with the breakdown of the three dimensional filler transient network. This phenomenon is sometimes known as a hysteretic process [4].

Effect of carbon black specific surface area (particle size)

In this section, the influence of carbon black surface area (or particle size) on viscoelastic properties of HNBR vulcanisates at a given black loading of 60 phr is focused. **Fig. 4** exhibits G′ rise with increasing carbon black surface

area, which could be explained by the greater contacting area available for interaction between rubber and carbon black as well as between filler particles (or three-dimensional transient filler network). It must be noted that, although N550 carbon black possesses lower specific surface area than N326 carbon black, the vulcanisate with N550 shows comparable G′ to that with N326. This phenomenon is explained by the relatively high crosslink density in the vulcanisates with N550 carbon black as evidenced by the high value of torque difference (i.e., the discrepancy in torques between maximum and minimum torque determined from cure curves) [12] as shown in **Fig. 5**. Such high crosslink density found in the vulcanisates with N550 is believed to cause a large amount of tightly bound rubber, which has been reported to obstruct the curative absorption on filler surfaces. This means a migration of free curatives to the free rubber matrix is promoted leading to the increased crosslink density [13]. It is also obvious that G′ of the vulcanisate with N550 show less strain dependence than that with N326, supporting the effect of crosslink density. The results of G″ as a function of strain amplitude are presented **Fig. 6**. It is evident that the strain-dependent G″ is clearly observed in all cured compounds with the greater magnitude found in compounds filled with carbon black having higher surface area. At deformation strain smaller than 30%, except for N990 thermal black having small surface area, the G" appears to decrease with strain due to the disruption of transient filler network. The specimens with high surface carbon black demonstrate high G" due to the high magnitude of filler network as discussed previously in **Fig. 2**.

The somewhat increase in G" at high strain is attributed to the viscous dissipation via molecular flow after the filler network is broken up.

Fig. 7 reveals the tanδ results of HNBR vulcanisates in a way that tanδ increases as the specific surface area of carbon black increases. As mentioned in carbon black loading effect, the increase in contacting area (by increasing surface area in this case) available for physical interaction between rubber and carbon black would lead to the rise in energy dissipation via molecular flow at carbon black interfaces. Again, the increment in tanδ as a function of strain is due to the disruption of filler network facilitating the molecular mobility of HNBR molecules. The strain onset for the rise in tanδ is smaller in the specimens with lower surface areas.

3.2 Heat build-up (HBU) behaviour

As mentioned earlier, the high applied stress is required to measure heat-build up (HBU) behaviour of HNBR vulcanisates having high modulus designed for the roll-covering applications to be used in steel and paper mills. A specially designed flexometer capable of offering high load applied to the test specimens is required. In this work, the Gabometer 4000 was utilised. **Fig. 8** reveals the HBU behaviour of black filled HNBR vulcanisates. By increasing carbon black loading, the HBU significantly increases, and the magnitude of HBU rise is more pronounced in the specimens with high surface area and/or structure. Such increase in HBU is anticipated to be the results of hysteretic process via the disruption of transient filler network and

molecular flow at the carbon black interfaces [8,9]. Exceptionally, the HBU is found to be highest in HNBR filled with N550, which is due probably to its relatively high extent of developed structure. At a given carbon black loading, the increase in surface area and structure of carbon black would increase filler transient network. Under deformation, these transient networks are disrupted, leading to the increase in hysteresis loss, and thus higher HBU in rubber vulcanisates.

From **Fig. 8**, it is clear that the HBU behaviour depends significantly on carbon black characteristics, and is needed to be measured for ensuring the acceptable performance of rubber product. However, the HBU measurement using the flexometer equipped with high load cell and powerful shaker is rather costly. Thus, one of objectives of the present work is to draw the correlation between viscoelastic results measured from oscillatory RPA2000 as a routine test and the HBU monitored from the specially designed flexometer. By this means, it is possible to estimate the HBU from the RPA2000 results. **Fig. 9** illustrates the relationship between loss modulus (G") as a hysteresis loss and HBU behaviour of cured HNBR (vulcanisates) filled with various carbon black surface areas. Evidently, regardless the carbon black characteristics, the HBU increases with increasing hysteresis loss, and their correlation to logarithmically agree well with the expression as shown in **equation (1)** with R^2=0.9115. In other words, the hysteresis loss plays strong role on HBU of HNBR vulcanisates studied. Apart from G", one might consider the loss factor (tanδ) as an indication of HBU at a given G' (or stiffness). **Fig. 10** reveals the change in HBU as a function of tanδ in a similar trend to that of

HBU against G" as illustrated in **equation (2)**, but with the lower R^2 of 0.8398. The results imply clearly that, as an indication of HBU under high load applied, the G" is superior to tanδ.

$$HBU = 18.019\ln(G'') - 61.971 \quad (1)$$

$$HBU = 33.907\ln(\tan\delta) + 102.83 \quad (2)$$

where HBU is Heat build-up as determined from the Gabometer 4000 while G" and tanδ are loss modulus and loss factor, respectively, as measured routinely from RPA2000.

CONCLUSION

HNBR vulcanisates with various carbon black loadings and characteristics (i.e., specific surface area and structure) were prepared. Viscoelastic properties as determined from oscillatory rheometer (RPA2000) were discussed. Heat build-up (HBU) behaviour was monitored using the stress-controlled flexometer equipped with high load cell (up to 4,000 N), namely, Gabometer 4000. Attempts to establish relationship among filler characteristics, magnitude of reinforcement and viscoelastic as well as HBU behaviours were made.

Results of viscoelastic behaviour demonstrate that, by increasing carbon black loading and surface area, elastic modulus (G') associated with damping

factor (tanδ) increases significantly. Mechanisms of carbon black reinforcement in HNBR are proposed as combined effects of hydrodynamic effect, filler transient network, molecular slippage at carbon black interfaces and crosslink density. Also, the HBU significantly increases with increasing carbon black loading and/or surface area, and the magnitude of HBU rise is more pronounced in the specimens with high surface area and/or structure. Lastly, it is possible to estimate the HBU generally measured from high-load flexometer from the RPA2000 results as a routine test; the G" is a more effective indication of HBU than tanδ.

ACKNOWLEDGEMENT

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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

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

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
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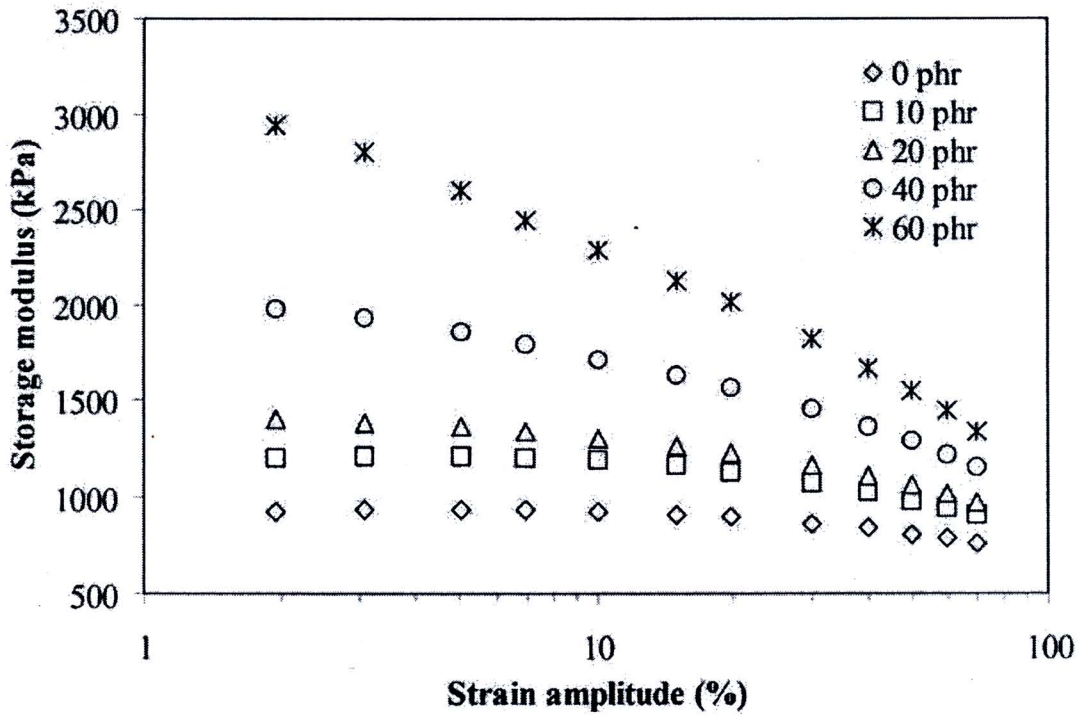

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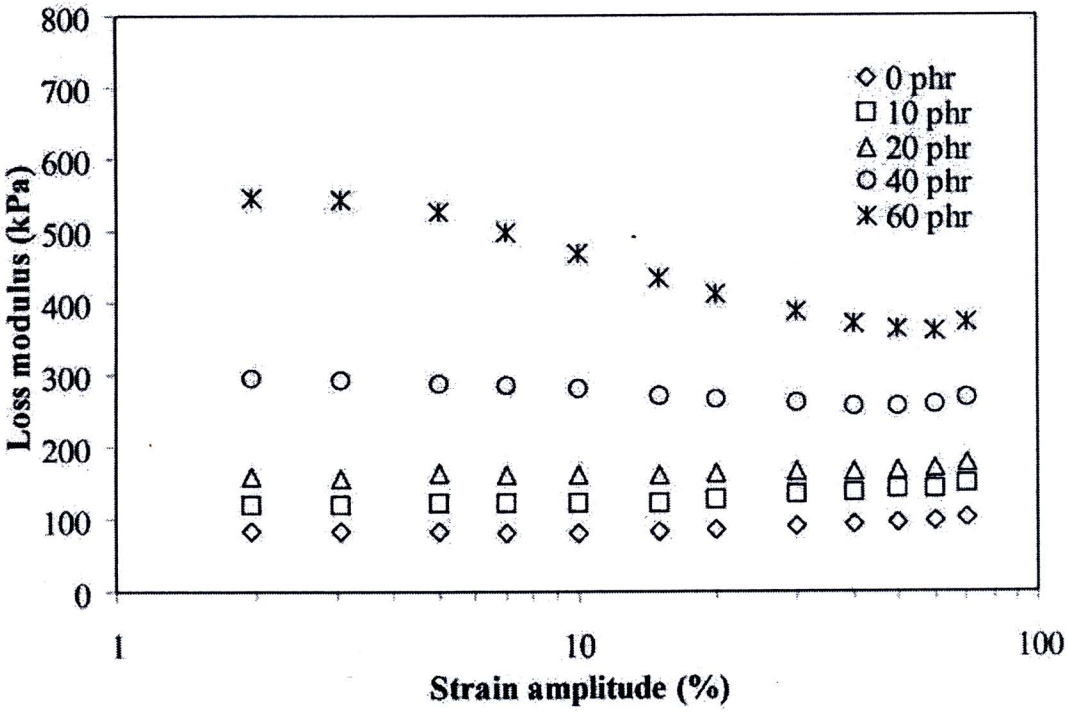

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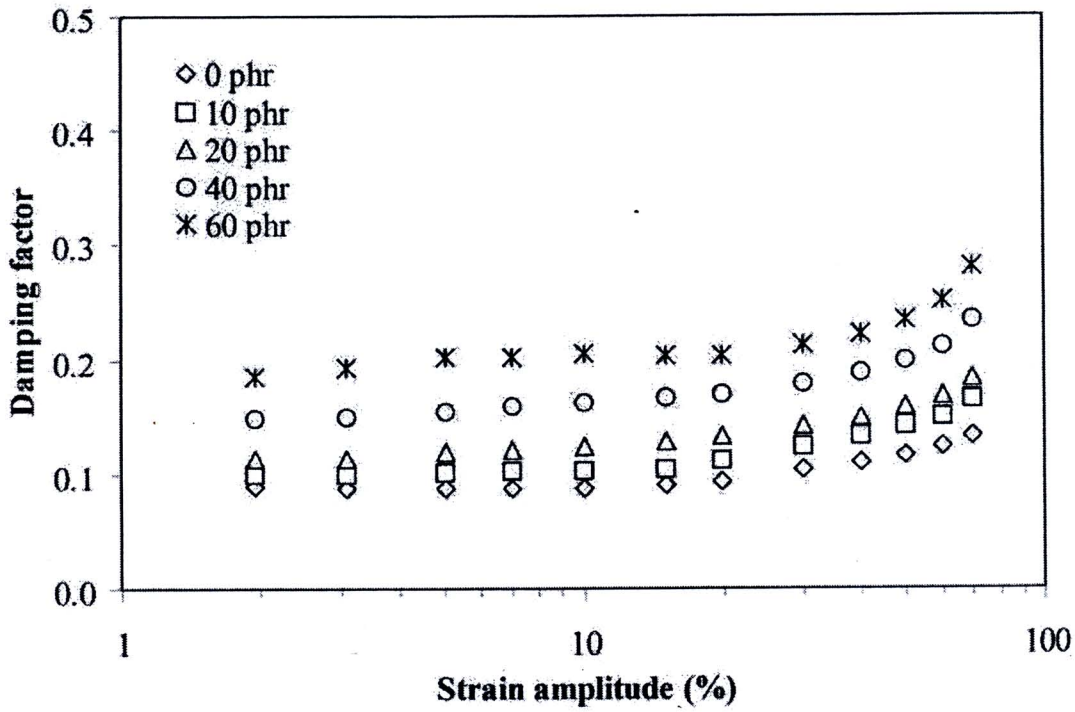

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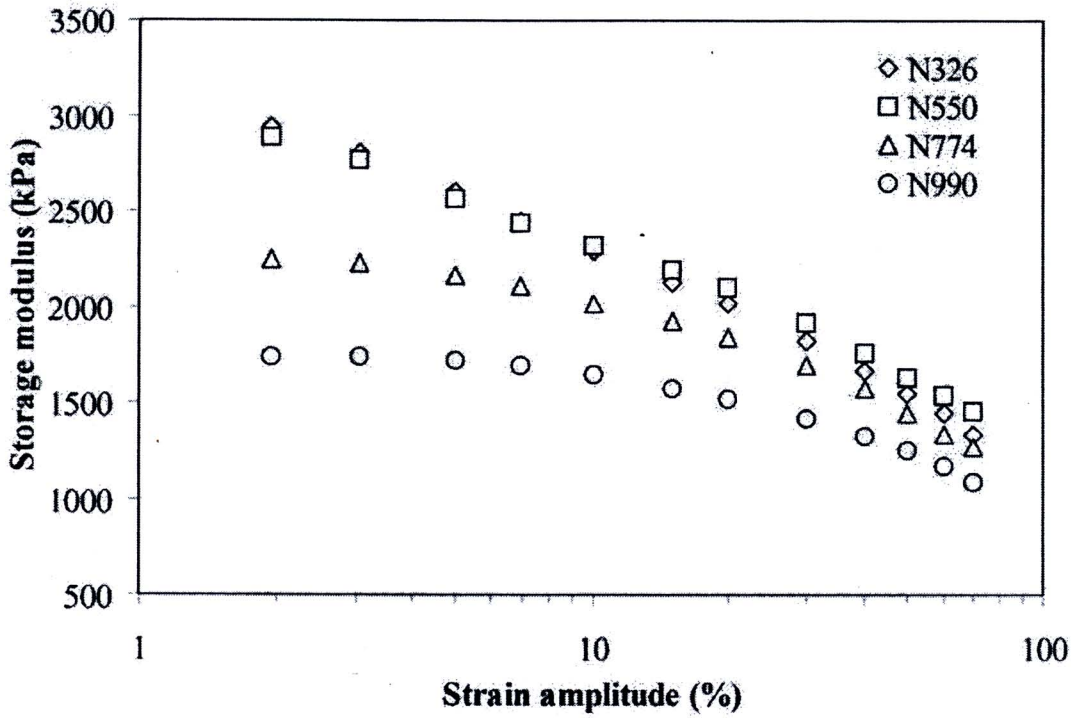

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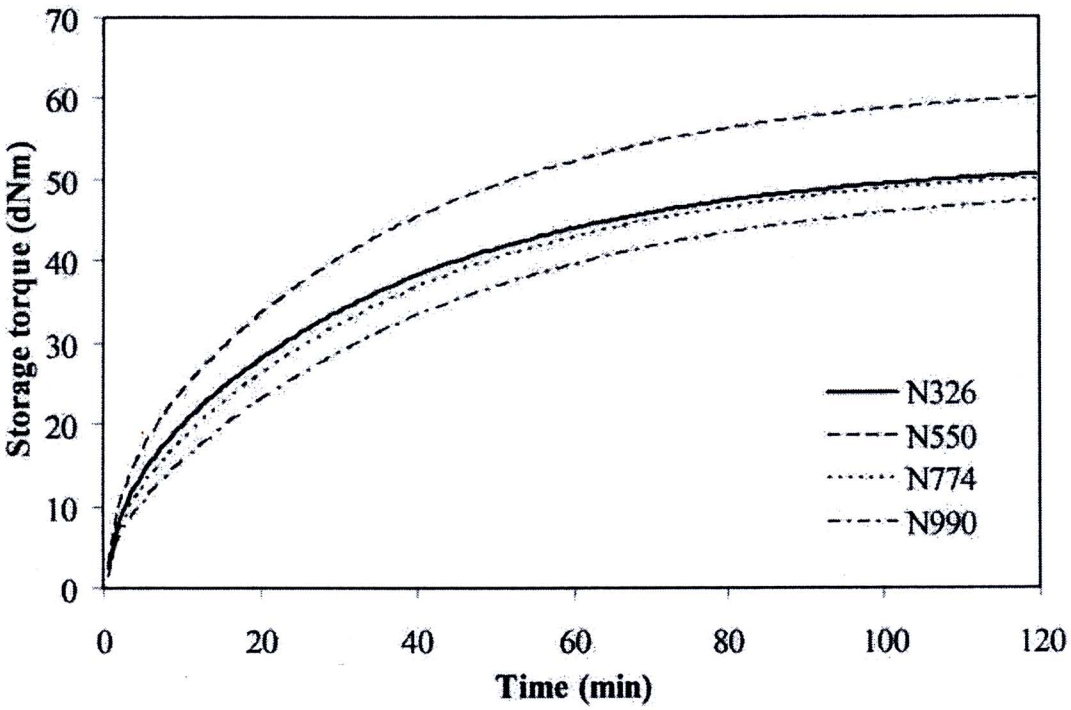

Figure 6
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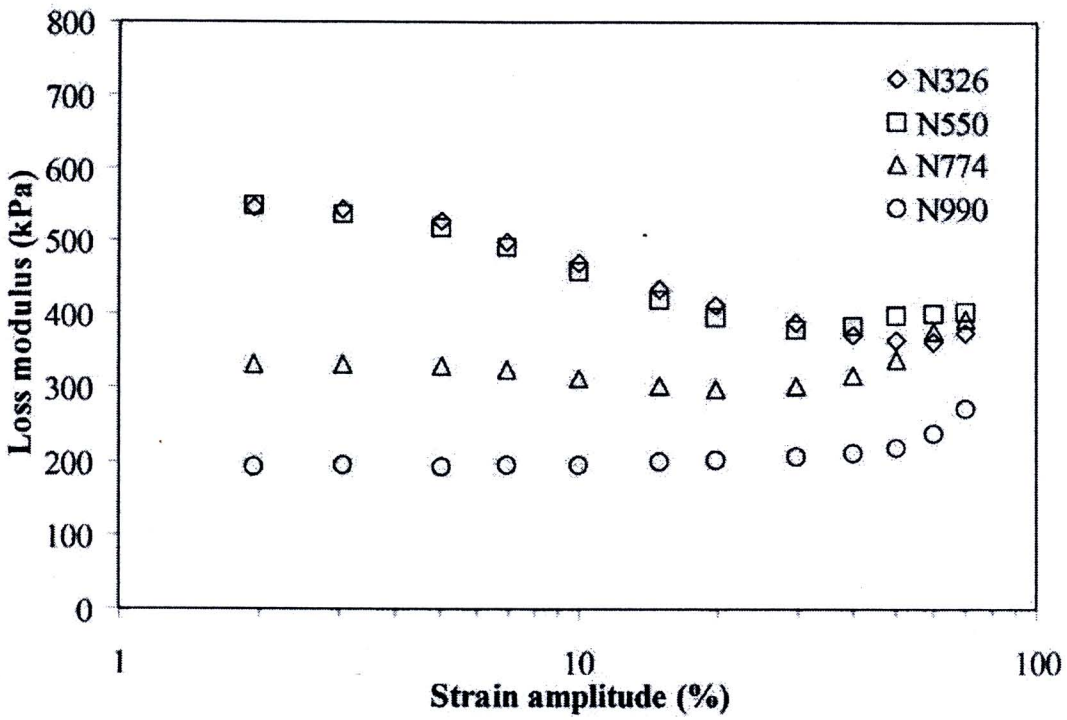

Figure 7
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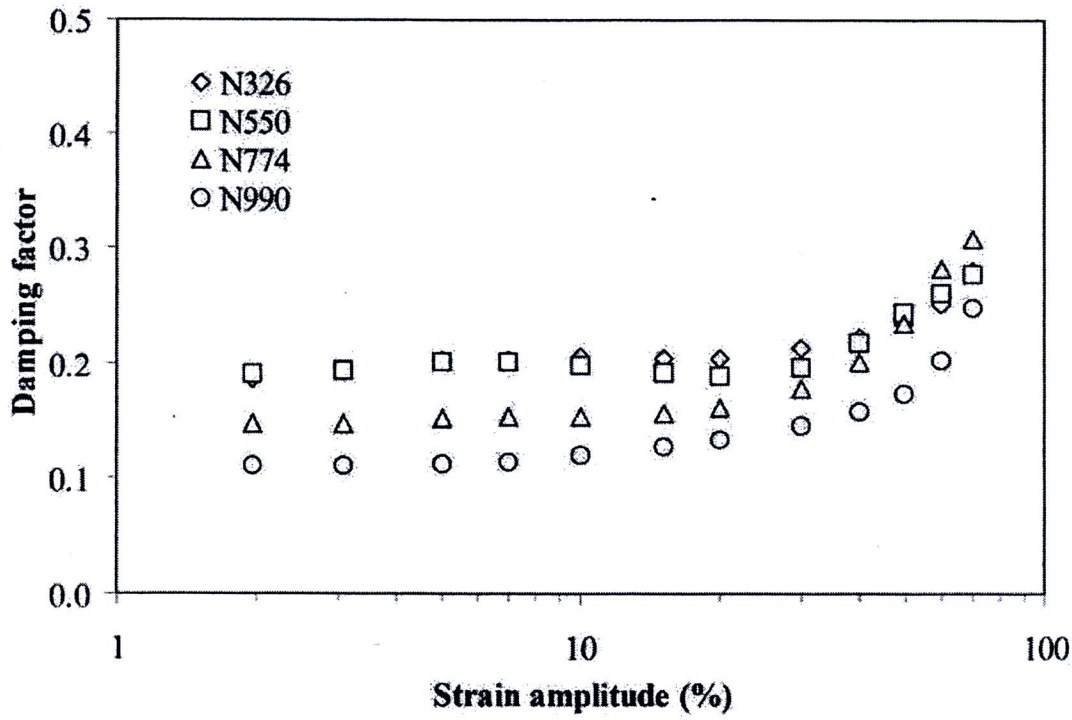

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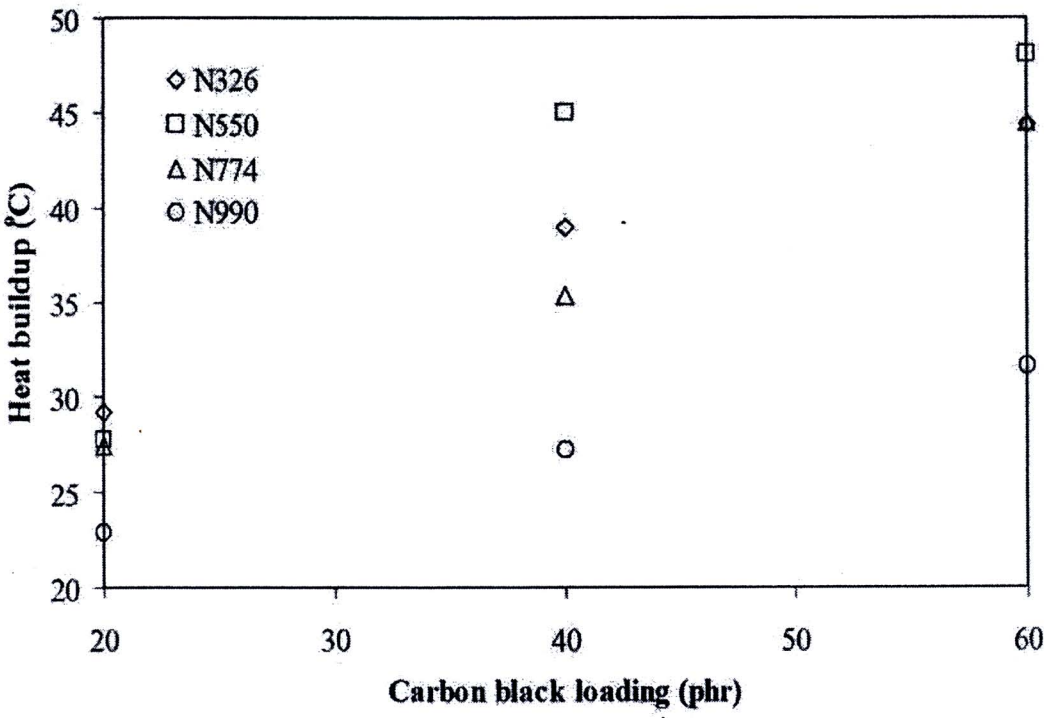

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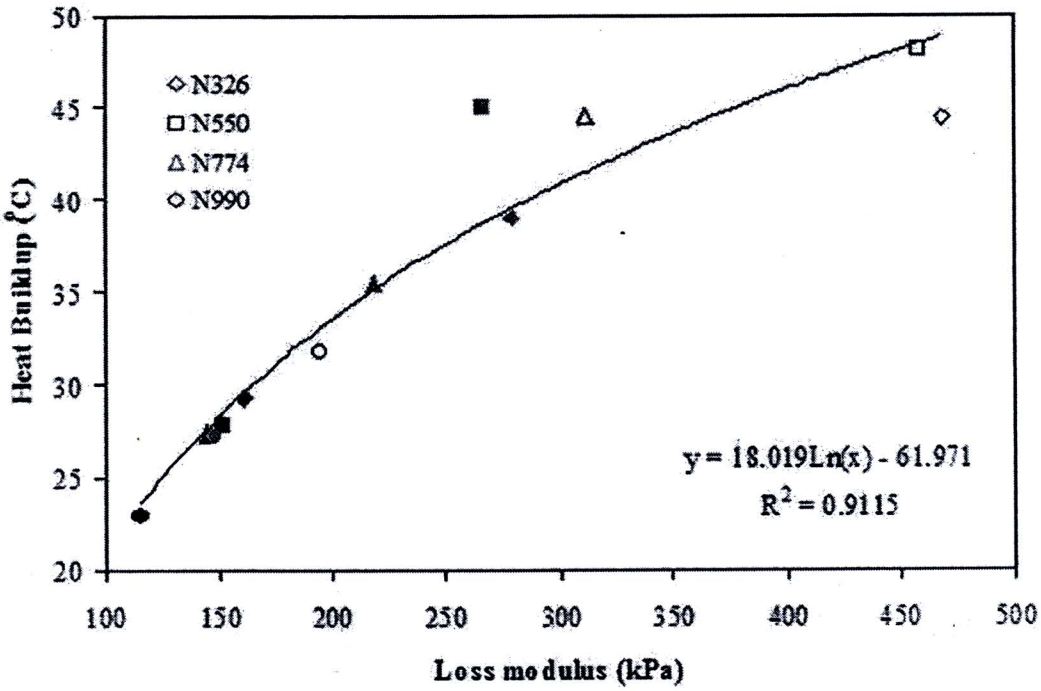

Figure 10
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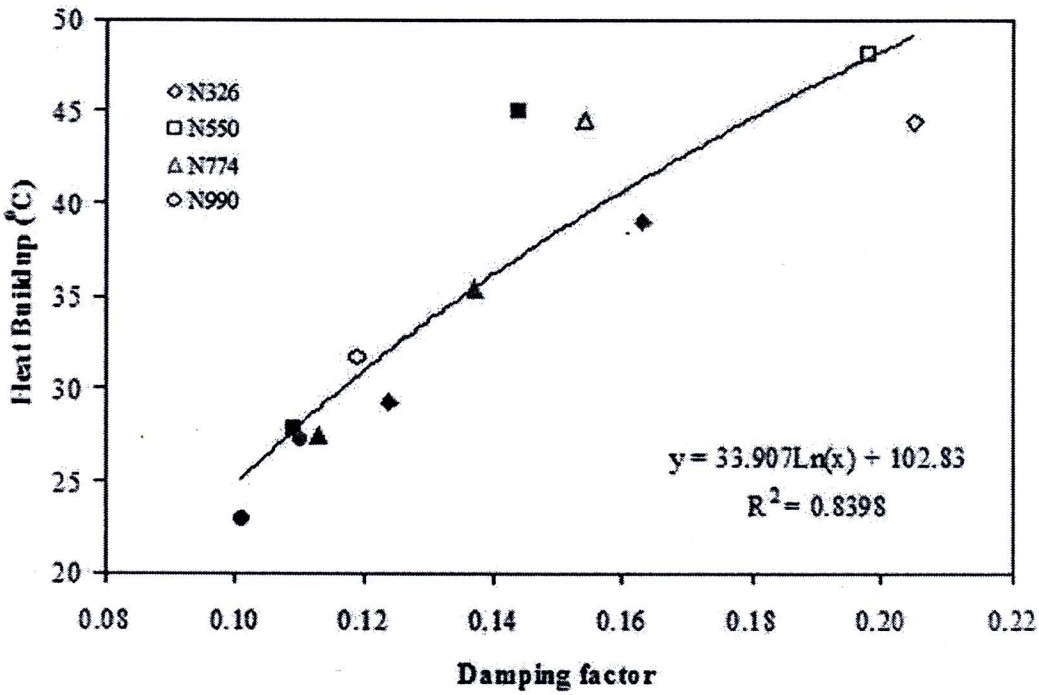

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Kautschuk & Gummi-Kunststoffe

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 (tanδ) 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 (tanδ) 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.

Cure and Viscoelastic Properties of HNBR

Effects of Carbon Black

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 tanδ 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).

Authors

P. Wongwitthayakool, C. Sirisinha, Bangkok (Thailand), P. Saeoui, Pathumthani (Thailand)

Corresponding author:
Chakrit Sirisinha
Mahidol University
Salaya Campus
RDCTRI, Faculty of Science
Phutthamonthon 4 Rd
Salaya, Nakhon Pathom, 73170,
Thailand
Tel: +662/441/0511
Fax: +662/441/9816
E-mail: sccsr@mahidol.ac.th

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/cm^2 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.

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].

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} m^3/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

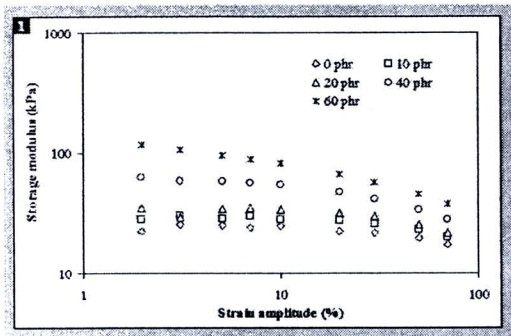
Viscoelastic properties

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-

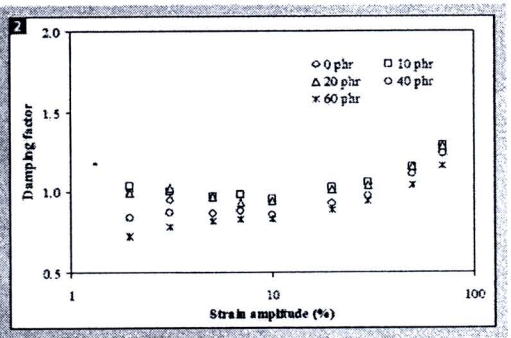
3 Cure characteristics of HNBR and filled HNBR

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

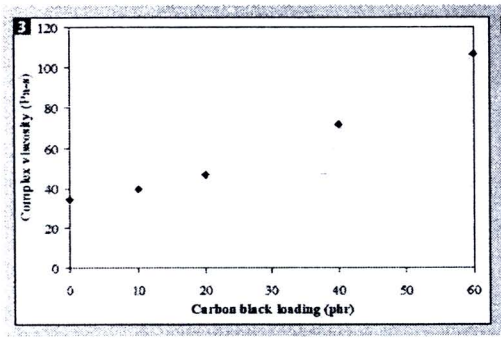
a = Torque difference between maximum (S'max) and minimum torques (S'min) as determined from cure curves



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)



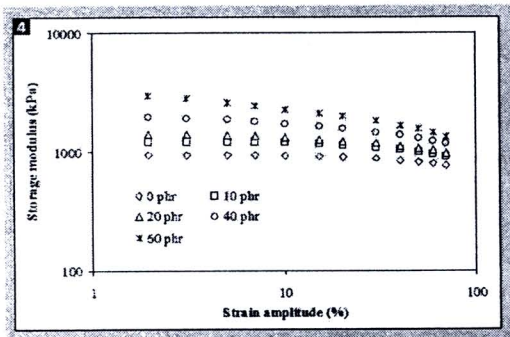
3 Complex viscosity (η^*) of uncured HNBR compounds as a function of CB N326 loading (measured at 1 rad/s, 10% strain and 100 °C)

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.

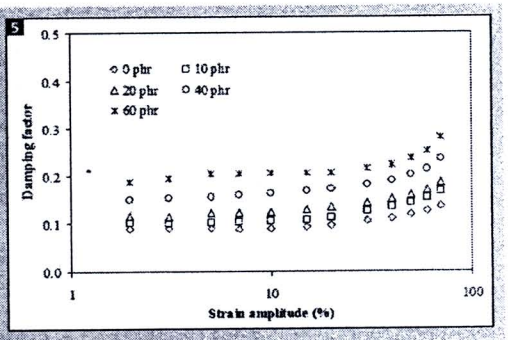
4 Mechanical properties of filled HNBR vulcanisates

Carbon black	Loading (phr)	M100 (MPa)	Tensile strength (MPa)	Elongation at break (%)	Hardness (shore A)	Abrasion loss (mm^3)
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

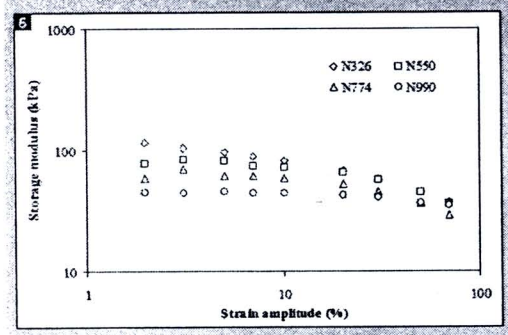
Results of damping factor (tanδ) are shown in Figure 2. It is obvious that the damping factor of all compounds increases with increasing strain amplitude. This is due to the energy dissipation through a molecular slippage associated with the breakdown of the three-dimensional filler transient network. 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



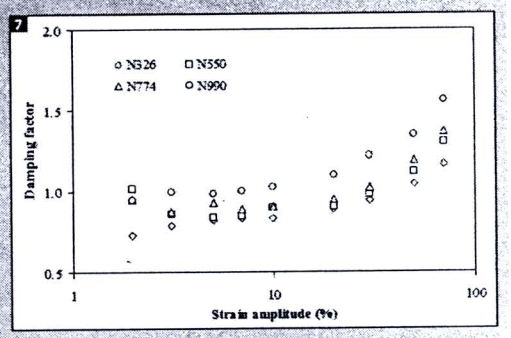
4 Storage modulus (G') as a function of strain amplitude of cured HNBR specimens (vulcanisates) with various CB N326 loadings (measured at 1 rad/s and 60 °C)



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.

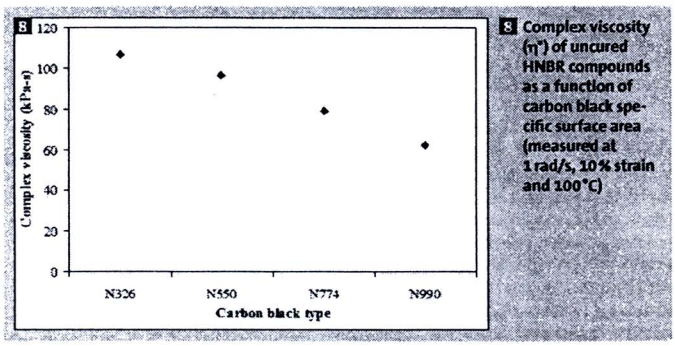
Cured HNBR vulcanisates

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.

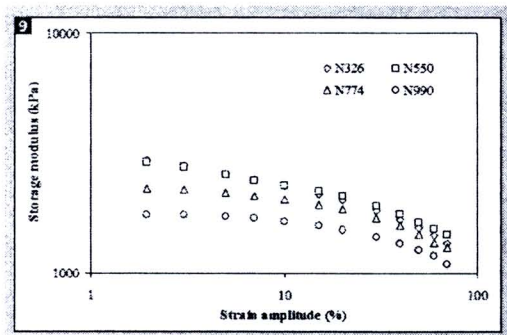
Cured HNBR vulcanisates

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.

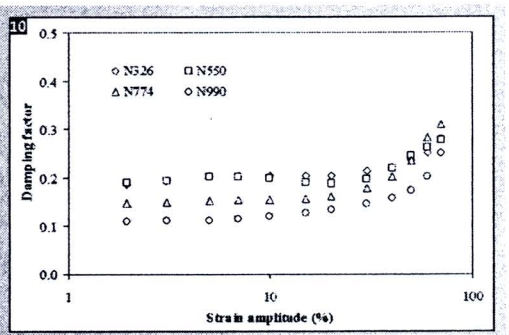
Figure 10 shows results of tanδ of filled HNBR vulcanisates. Clearly, tanδ increases with increasing carbon black specific surface area that means the higher energy dissipation through molecular flow at carbon black surfaces, as discussed previously in carbon black loading effect.

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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The authors

Ms. P. Wongwitthayakool is a Ph.D. research student in the Department of Chemistry, Faculty of Science, Mahidol University. Dr. P. Saeoui is a researcher at the National Metal and Materials Technology Center. Dr. C. Sirisinha is a lecturer in the Department of Chemistry, Faculty of Science, Mahidol University, and researcher based in the Research and Development Centre for Thai Rubber Industry at Mahidol University.

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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

คณะผู้วิจัยจึงต้องพยายามเรียบเรียงเนื่อหาบทความที่จะตีพิมพ์ในลักษณะที่ต้องประณีประณอม เช่น การตัดผลของบางตัวแปรออกจากบทความและหาข้อมูลส่วนอื่นมาแทนที่ ทำให้ใช้เวลาในการตีพิมพ์นานมากกว่าปรกติ อย่างไรก็ตามคาดว่าเมื่อทุกอย่างลงตัวน่าจะสามารถตีพิมพ์ผลงานในวารสารวิชาการได้อย่างน้อย 2 เรื่อง