Influence of carbon black with different concentration on dynamic properties and heat buildup of semi-efficient natural rubber composites

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High abrasion furnace black (HAF) filler has long been recognised as reinforcing filler, but the impact of concentration on dynamic mechanics performance and heat buildup of vulcanisates is rarely reported. Therefore, natural rubber (NR) composites filled by N330 with different concentration were prepared. Payne effect and heat buildup of HAF/NR composites increases with an increase of HAF loadings during to that filler network structure become stronger with an increase of HAF loadings. Moreover, tensile strength, tear strength as well as modulus increase with an increase of HAF loadings is attributed to better dispersion and improved interfacial interaction between HAF and NR matrices. The results reveal that composites with 60 per hundreds of rubber (phr) of HAF exhibit better overall mechanical properties and lower heat buildup.

1. Introduction: As we all known, natural rubber (NR) shows multitudinous significant performance, for instance, high strength, elevated wet grip and rolling resistance, low gas permeability, to some extent, these could match with the properties of synthetic rubbers [1]. Although NR shows multitudinous excellent features, upon most occasions, it is obligatory to add reinforcing fillers into NR to achieve some purpose of application. Granular packing is widely used for a variety of purposes in rubber industry, and reinforcement is foremost, and to reduce the material costs and improve the process [2]. To enhance the abrasion resistance, strength and strength-related properties, e.g. modulus and hardness, is called to reinforce composites [3, 4]. The carbon black (CB) is the most widely used reinforcing fillers in most applications owing to the outstanding properties it gives to vulcanisates [5]. There are many functional groups, for instance, ketone, carboxyl and aldehyde hydroxyl, on the surface of CB [6, 7]. The tear strength, tensile strength, abrasion resistance and modulus of vulcanisates increase when CB is compounded with rubber. Therefore, CB is widely used in the rubber industry products [8].

The cross-link density initially increased after the thermal-oxidative aging. The result shows that the elongation at break of all the samples decreases after aging. It is mainly due to the incremental cross-linking after aging for all the vulcanisates, and it is well known to us as post curing effect. The mobility of rubber chains reduces because of an increase of the cross-linking density via the post curing [9–11]. In spite of several past studies has been made to elucidate mechanical properties of composites with different concentrations of HAF, since the introduction of the so-called 'Green tire' by Michelin, the dynamic mechanics performance and heat buildup of vulcanisates become more important, however, the effect of different concentrations of HAF on the dynamic mechanics performance and heat buildup of vulcanisates is rarely reported. Therefore, NR composites filled by N330 with different concentration were prepared and investigated in detail. The cure characteristics, morphological, dynamic mechanics performance and heat buildup of NR were investigated and discussed.

2. Experimental

2.1 Materials: NR was provided by Hainan Agricultural Reclamation Co., Ltd. Other mixing ingredients, e.g. N-(oxidiethylene)- 2-benzothiazolyl sulfenamide (NOBS), zinc oxide, stearic acid, N-isopropyl-N'-phenyl-4-phenylenediamin (4010-NA), poly(1,2-dihydro-2,2,4-trimethyl-quinoline) (RD) and sulphur (S) were provided by Shijiazhuang Zhongshan Chemical Co., Ltd. High abrasion furnace black (HAF) was provided by China Rubber Group Carbon Black Research Institute, the average particle size and particle size of the aggregate of HAF particles are 29 and 154 nm, respectively.

2.2 Preparation of vulcanisates: Table 1 shows the compounding formulations, and it is based on changing concentration of CB. The composites are named as Nx, and the x is the amount to the portion of HAF. The formulation of composites is expressed as portion per hundreds of rubber (phr), and the basic formula is listed as: NR 100, ZnO 5, SA 2, 4010NA 1, RD 1, HAF variable, NOBS 2, sulphur 2. Other ingredients were blended with NR at 110°C for 15 min, in the internal mixer, except the curatives. Then the curatives were blended with the compounds below 40°C, on a two roll-mill, and compression moulded at 150°C under the optimum cure time of samples, which were obtained from a TD-6019 No-rotor Rheometer following ISO 6502.

2.3 Determination of cross-link density: The equilibrium swelling method was applied to study the cross-link density. Samples initially were extracted with acetone for 24 h in a Soxhlet apparatus for the sake of removing substances like remains of activators and accelerators and dried at 50°C in a vacuum oven. Then put the samples into n-heptane at room temperature to swell for 48 h, and then weighed the swollen samples and dried at 50°C in a vacuum oven to a constant weight. The cross-link density was counted on the basis of Flory–Rehner [12–16].

2.4 Cross-link distributions: Thiol/amine reactants were used to measure the cross-link distributions of vulcanisates [17–20]. To selectively cleave polysulphidic cross-links, 0.4 M 2-propanethiol and 0.4 M piperidine in n-heptane solution was used at room temperature for 2 h. To break the polysulphidic crosslinks and disulphidic cross-links, 1 M 1-hexanethiol in piperidine was applied at room temperature for 48 h. The discrimination between the di-, mono- and polysulphidic cross-links can be determined from the combination of these two treatments. Samples were

Table 1 Compound formulations

Ingredients, phr[a]	Sample				
	N30	N40	N50	N60	N70
NR	100	100	100	100	100
zinc oxide	5	5	5	5	5
stearic acid	2	2	2	2	2
RD[b]	1	1	1	1	1
4010NA[c]	1	1	1	1	1
HAF (N330)	30	40	50	60	70
NOBS[d]	2	2	2	2	2
sulphur	2	2	2	2	2

[a]Part per hundred parts of rubber.

[b]Poly(1,2-dihydro-2,2,4-trimethyl-quinoline).

[c]N-isopropyl-N'-phenyl-4-phenylenediamin.

[d]N-(oxidiethylene)-2-benzothiazolyl sulfenamide.

washed by dipropylmethane for three times, and extracted for another 24 h in acetone and then dried at 50°C in a vacuum oven to a constant of weight. Equilibrium swelling was used to measure the sum of di- and mono- and the mono-cross-link densities of the samples, which are treated by the chemical probes, and the mono-, di- and polysulphidic cross-link densities can be obtained by a subtraction from the total value of cross-link density, separately.

2.5 Mechanical characterisation: We measured the hardness, tear strength and tensile strength properties of all the composites in accordance with ISO 34-1, ISO 37 and ISO 48, respectively. The cross-head rate for tensile testing was 500 mm/min with an initial clamp separation of 65 mm. The specimens were aged to study the heat aging resistance for 22 h at 100°C in a circulating air chamber. The aged specimens were left at room temperature for at least 18 h before testing.

2.6 Scanning electron microscopy (SEM): To examine the fracture surfaces of vulcanisates, a Hitachi Su-1500 scanning electron microscope was applied. Samples, to prevent charging on the surface, were sputtered with gold before the examination.

2.7 Dynamic rheological properties (RPA): RPA 2000 was used to analyse the dynamic rheological performance of composites at 60°C (USA, Alpha Technologies Co.). For the compounds, at the test frequency of 1 Hz, the range of strain amplitude is from 0.28 to 400%. For vulcanisates, the frequency is 10 Hz, the range of strain amplitude is from 0.28 to 100%.

2.8 Heat buildup study: Goodrich Flexometer Model YS-III was used to measure the heat buildup of composites based on ISO 4666. A compressive load of 245 N was imposed on the samples preheated for 30 min at 55°C with frequency of 20 Hz, amplitude of 4.45 mm and test time of 25 min. At the base of samples, the increase of temperature was recorded.

3. Results and discussion: Viscosity of the compound increases for several reasons when CB is added to raw rubbers, such as the structure which is related to anisometry of filler aggregates for CB, the hydrodynamic effect for CB loading, rubber molecules is treated as bound rubber or as shell of immobilised rubber which is adsorbed on the filler surface and the occlusion of rubber within the aggregates. The movement for whole molecules in a flow field is restricted once the portion is fixed on the surface of filler. Follow the joint shell mechanism filler network might be formed when CB is commendably wetted with rubber [21–24].

3.1 Rheological properties: The physical property for elastomeric material is strongly influenced by filler morphologies, e.g. structure, essentially surface characteristics and particle size. The chemical active sites and the surface characteristics are the most important parameters and it determines the interaction between polymer chains and filler [25]. Fig. 1 shows the rheological characteristics of composites filled with HAF. The minimum torque (M_L) is considered as a measure of filler–filler inner aggregate formation for filled vulcanisates and it reflects minimum viscosity of compound.

It shows that M_L, the minimum torque, gradually increase up to 60 phr HAF then increases faster when add extra HAF. It is attributed to filler network structure which forms among CB aggregates. The cross-link density of the samples can be roughly measured by the difference between M_H and M_L and it is usually known as Δt [26]. We can see that Δt increases with an increase of HAF concentration. The reinforcement or filler–rubber interaction can be characterised by changes of rheological torque with filler loading. It is attributed improved physical and mechanical properties of vulcanisates during to the planned choice of the smallest particle sizes. The difference between the scorch time t_{s2} and optimum curing time of vulcanisates t_{c90} can be used to measure the rate of vulcanisation, and the CRI (cure rate index) can be calculated by the following equation [27]

$$\text{CRI} = \frac{100}{t_{c90} - t_{s2}} \qquad (1)$$

Fig. 1c shows obviously that the CRI increases with increasing content of HAF when HAF content is less than 40 phr and then become nearly constant, and then increases with increasing the HAF content for the sample more than 60 phr. It may be a result of the decrease in t_{c90} of composites greater than corresponding t_{s2} and this may be put down to pre-cross-linked (physical cross-linking for the bound rubber) and strong interfacial rubber–filler interaction.

3.2 Cross-link structure: CB is the mainly applied reinforcing fillers for rubber industry. The shapes and sizes of primary aggregates of CB influenced by concentration are directly related to physical properties of reinforced rubber [28]. Table 2 shows the cross-link structure of composites. We can see that cross-link density increases with an increase of HAF content. It is attributed that more cross-links are formed nearby fillers [29], and consequently
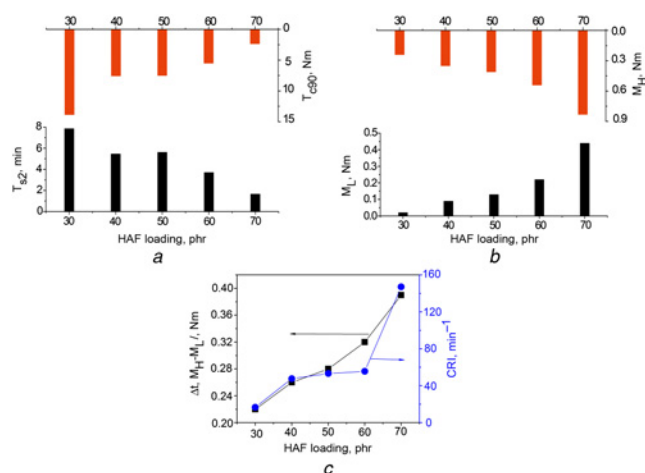
Fig. 1 *Vulcanisation characteristics of composites*
a The scorch time t_{s2} and optimum curing time t_{c90}
b The minimum torque (M_L) and maximum torque (M_H)
c The difference between M_H and M_L, the CRI (cure rate index)

Table 2 Cross-link structure of composites ($\times 10^{-4}$ mol/cm^3)

Sulphidic cross-link density		30	40	50	60	70
unaged	overall	1.59	2.66	2.90	3.91	4.41
	poly	1.04	1.65	1.81	2.47	2.29
	mono and di	0.55	1.01	1.09	1.44	1.42
aged	overall	1.81	2.71	3.11	3.99	4.92
	poly	1.19	1.60	2.01	2.46	3.41
	mono and di	0.62	1.11	1.10	1.53	1.51

the filler–rubber interaction will be increased. On the basis of Lorenz and Parks [30], the interaction between rubber and filler was calculated and studied. In addition, all the cross-link densities increase after aging during to a small degree of swelling as reported [9].

3.3 Mechanical properties: The distribution of the HAF in matrix decides the hardness and the hardness increases with an increase of HAF content. As we all know that the elasticity of polymer chains decreases when join filler particles into soft matrix and more rigid vulcanisates are obtained. As clear from Table 3, the addition of black filler shows an obviously increase of hardness for filled composites which reflects an improved stiffness. It is attributed that more HAF is put into matrix and HAF particles have relatively higher modulus. The flexibility of the polymer chains is decreased and composites become more rigid. We know that the hardness of materials show a linear increase when add filler into rubber compound; moreover, the elastic modulus is also correlated to the international rubber hardness [10].

After thermal-oxidative aging, the modulus and surface hardness show similar behaviours. It indicates that the surface hardness change depended principally on the elasticity degradation of the skin layer with aging time [9]. To some degree, the surface harnesses can give the changing behaviour in modulus because of the similarity.

The rupture path of stress distribution within rubber mainly decides tensile strength of composites. For a given CB, to achieve the highest possible tensile strength a strong filler–rubber interaction is essential so that to maximise micro-dispersion is significant [31]. From Figs. 2a and b, we can see that tear strength and tensile strength of composites increase obviously with an increase of HAF concentration and it indicates the reinforcement effect of HAF.

After aging, when the concentration of HAF is 30 phr tear strength and tensile strength of vulcanisates increase as a result of the increased cross-link density as mentioned above. However, that of other composites decreases because the value of cross-link density is more than the best cross-link density values as reported. As we all known, there are two cross-link densities for each vulcanisates, respectively, corresponding to the best tensile strength and best tear strength of each vulcanisates. The cross-link density for the best tensile strength is larger than that of the best tear strength.

Table 3 Modulus and hardness of aged and unaged NR compounds

HAF loading, phr		30	40	50	60	70
unaged	100% modulus, MPa	1.11	1.96	2.32	3.13	4.17
	300% modulus, MPa	5.00	8.84	10.54	14.17	17.98
	hardness, (shore A)	51	61	67	69	75
aged	100% modulus, MPa	1.46	2.94	3.01	4.87	6.91
	300% modulus, MPa	6.77	13.29	12.91	15.44	–
	hardness, (shore A)	57	66	69	72	78
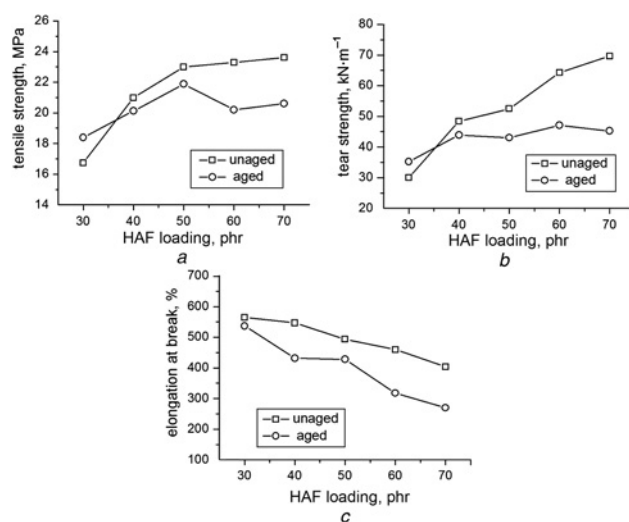
Fig. 2
a Tear strength
b Tensile strength and
*c* Elongation at break of composites

Results in Fig. 2, the cross-link density of vulcanisates is larger when the concentration of HAF is more than 30 phr, especially after aging, the cross-link density of vulcanisates is larger than the cross-link density of vulcanisates for the best tensile strength so that both tensile strength and tear strength reduced with increasing HAF loading. The cross-link density of vulcanisates is smaller when the concentration of HAF is 30 phr, after aging the cross-link density increased and it was much closer to the cross-link density for the best tear strength.

Fig. 2 shows the mechanical properties of composites. We can see that these small particle sizes HAF have better dispersion and the strong filler–rubber interaction plays a role in the improved performance of vulcanisates. It suggests that the size and structure of added CB were the main factors. These improvements of tear strength and tensile strength can be attributed to strong interactions of filled composites at the boundaries, on account of HAF dispersion and even for intercalated morphologies [31]. After aging, the cross-link density increased because of post vulcanisation so that the motility of macromolecular chain reduced, and the elongation at break of composites all decreased.

3.4 Micromorphology of composites by SEM: Tensile fractured surfaces of composites are characterised by SEM to analyse this significant improvement in mechanical properties. As shown in Figs. 3a–e, it is obvious that surfaces for HAF/NR composites became much rougher and have more protuberances with an increase of HAF loadings. Since the better dispersion of HAF reduces the stress concentration and the stronger interaction between HAF and NR is conducive to the propagation of stress, and the tensile strength became much higher with increased HAF loadings.

3.5 Heat buildup: Heat buildup of all composites is compared in Table 4 and the heat buildup is the difference value of temperature at the bottom of the cylindrical sample before and after testing. The results show that heat buildup progressively increases with an increase of HAF loadings. Since more cross-links nearby fillers are formed and consequently stronger filler–rubber interaction is constructed. As mentioned previously, the content of bound rubber increases with an increase of HAF loadings so that the inner rub between HAF and polymer increase, and the free volume decrease in the process of test.
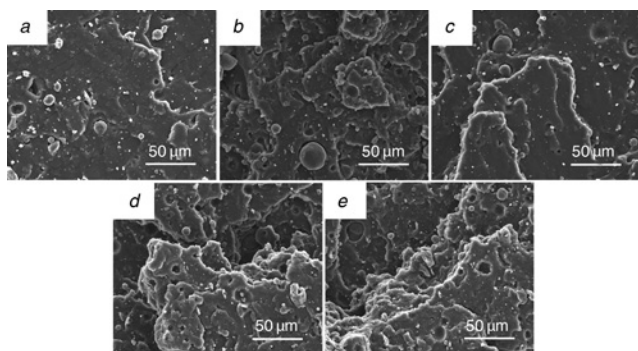
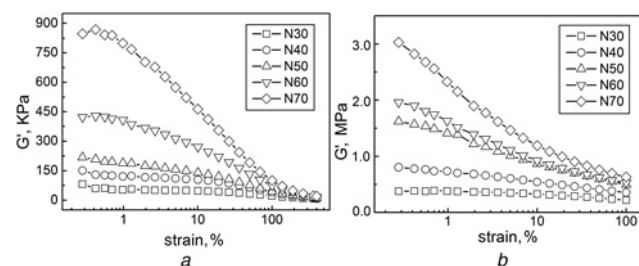**Fig. 3** *SEM photos of fracture surface of composites*
a N30
b N40
c N50
d N60
e N70

Table 4 Heat buildup of the vulcanisates

HAF loading, phr	30	40	50	60	70
heat buildup, °C	11.5	12.0	15.1	17.4	19.7

Fig. 4 *a and b curves of G′ versus strain of compounds and vulcanisates*

3.6 Dynamic mechanics performance by RPA: According to the report, various factors govern the relationship between the shear strain and storage modulus of vulcanisatesis, for instance, rubber network properties, filler–rubber interaction and strong filler–filler interaction. However, the interaction of filler–filler increase and it is the main factor for the increase of storage modulus at the small strains. Therefore, to study the filler network structure in this experiment, the relationship between shear strain and storage modulus is studied. As shown in Fig. 4, Fig. 4*a* shows the variation of G' with strain of compounds and the variation of G' with strain of composites is represented in Fig. 4*b*. Payne effect is the strain dependence of the dynamic viscoelastic properties, regarding as storage modulus in a filled rubber compound and vulcanisates [32–34]. The weaker filler network of rubber matrix and the higher filler dispersibility will lead to lower Payne effect. Payne effect of HAF/NR compound increases when there is an increase of HAF loadings as shown in Fig. 4*a*. The G' of composites from Fig. 4*b* has the same variation strain dependence tendency as that of compounds from Fig. 4*a*. The G' of a HAF/NR composites is lower than that of HAF/NR compound mainly related to strong molecular interactions and filler–rubber interactions [35, 36]. In addition, the filler network structure in HAF/NR composites becomes stronger with an increase of HAF loadings, which is consistent with the heat buildup presented above.

4. Conclusions: The influence of HAF loadings on the performance of NR composites has studied in this Letter, especially the dynamic mechanics performance and heat buildup.

The curing rate is enhanced with an increasing HAF concentration of vulcanisates, however, t_{s1} and t_{s2} decrease, and the torque values are increased with HAF loading. The increasing HAF loading of vulcanisates leads to the pronounced increase of tear strength and tensile strength, moreover, significantly elongation at break decreases with increasing HAF concentration during to the stronger rubber–filler interaction and increased cross-link density. Especially after aging, the cross-link density increased because of post vulcanisation so that the motility of macromolecular chain reduced, and the elongation at break of all the composites decreased. The Payne effect and heat buildup in HAF/NR composites increase with an increase of HAF loadings during to that more cross-links are formed nearby fillers because of the stronger filler–filler interactions, filler–rubber interactions and molecular interactions. After thermal-oxidative aging, an obvious increase in modulus and hardness of the rubber with HAF is mainly related to the elasticity degradation of the skin layer. The investigation reveals that vulcanisates exhibit better overall mechanical properties and lower heat buildup when the content of HAF is 60 phr.

6 References

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