Experimental Analysis of Viscoelastic Properties in Carbon Black-Filled Natural Rubber Compounds

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ABSTRACT: Processability and viscoelastic properties of natural rubber (NR) compounds filled with different carbon black loadings and types were investigated with the use of a steady shear rheometer, namely, the Mooney viscometer, and an oscillatory rheometer, namely, the Rubber Process Analyser (RPA2000). It was found that the type and amount of carbon black strongly influence the viscoelastic properties of rubber compounds. Both the dilution effect and filler transient network are responsible for the viscoelastic properties, depending on the vulcanization state. In the case of uncured compounds, the damping factor of the uncured NR decreases with increasing black loading. This is attributed to the reduction of mobilized rubber content in the compound (or the dilution effect). However, in the case of the cured NR vulcanizates, the filler transient network is the dominant factor governing the damping factor of the vulcanizate. With increasing black loading, the damping factor of the vulcanizate clearly increases. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 2197–2203, 2005

Key words: carbon black; dynamic mechanical properties; natural rubber; viscoelastic properties

INTRODUCTION

Dynamic behavior of filled rubber is of key importance in the performance of rubber engineering products or structural components, such as tire treads, tank pads, building mounts, automotive suspensions, and engine mounts.[1,2] The dynamic properties are usually expressed in terms of the complex modulus, which consists of a storage modulus and a loss modulus. A storage modulus or in-phase component represents an immediate response to the application of the force. A loss modulus or out-of-phase component represents the energy dissipated as heat. The ratio of the former to the latter is generally known as a damping factor (tan δ), which is a measure of the energy dissipated by various processes, such as molecular mobility,[3,4] breakdown and reformation of the filler transient network,[4] or slippage of rubber molecules under high strain amplitudes.[5] In addition, a good correlation has been found between damping factor and some properties that are classical for designing engineering products, namely, noise, damping, and acoustic behavior. For example, the vibration damp of car tire treads could be increased by increasing damping factor.[6,7] On the negative side, some parts of the dissipative energy, which are not easily conducted away, are transformed into heat and, therefore, deteriorate rubber vulcanizates. Medalia[3] reported that, with increasing temperature in rubber products, fatigue life of the rubber component decreases drastically. Therefore, the optimal damping factor is one of the important factors to which much attention should be paid in developing products. Numerous works reveal that the damping factor depends markedly on types of rubbers,[8] fillers,[9–14] the extent of interactions between filler and rubber matrix,[9,15,16] strain magnitude,[10,15,17] and temperature.[9,18,19] However, there are not many works reporting a comparison of dynamic properties between uncured and cured elastomers filled with carbon black. This became the main objective of the present work, which was to compare the effects of carbon black loading and type on dynamic properties in uncured and cured natural rubbers.

EXPERIMENTAL

Materials

Details of compounding ingredients and rubber formulas used are shown in Table I.

Mixing and vulcanization procedures

Mixing was carried out using a local-made 0.5 L Banbury internal mixer with fill factor, rotor speed, and set temperature of 0.7, 40 rpm, and 40°C, respectively.

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TABLE I
Compounding Ingredients Used in the Present Study

Chemical name	Amount (phr)	Grade/Supplier
Natural rubber (NR)	100.0	STR 5, Thailand
Carbon black	varied	N220, N330, N550, N660/Thai Carbon Product Co. Ltd., Thailand
Sulphur	2.5	Commercial/Chemmin Co. Ltd., Thailand
Stearic acid	2.0	Commercial/Chemmin Co. Ltd., Thailand
Zinc oxide	5.0	Commercial/Chemmin Co. Ltd., Thailand
Paraffinic oil	10	Flexon 845/Exxon Co. Ltd., Thailand
TBBS[a]	1.0	Santocure, TBBS/Flexsys Co. Ltd., Akron, OH
6-PPD[b]	1.5	Santogard, 6PPD/Flexsys Co. Ltd., Akron, OH

[a] *N*-tert-Butyl-2-Benzothiazole sulfonamide.
[b] *N*-(1, 3-Dimethylbutyl)-*N*′-Phenyl-P-Phenylenediamine.

Natural rubber (NR) with an initial Mooney viscosity at 100°C of 72 was first charged to the mixer and masticated for 3 mins, followed by the addition of cure activators (i.e., stearic acid and ZnO) and amine-based antioxidant (i.e., 6-PPD). Mixing was continued further for 2 mins, and then half of the carbon black was added and mixed for 2 mins. The other half was thereafter added with oil and mixed further for 6 mins. Sulfur as a curing agent and TBBS as a cure accelerator were then charged and mixed for 2 mins. Finally, the compound was dumped, sheeted on the cold mill, and kept at room temperature for 24 h before testing.

Measurement of Mooney viscosity and Mooney relaxation

Mooney viscosity and Mooney relaxation of rubber compounds were determined using the Mooney viscometer (Techpro model ViscTech+) with a large rotor at a test temperature of 100°C. The Mooney viscosity was determined according to ASTM D1646 and reported in Mooney units (MU). Analysis of stress relaxation data (Mooney viscosity versus time data) is based on ASTM D1646.

Measurement of bound rubber content

Rubber compounds to be determined for bound rubber content weighing approximately 0.2 g were immersed in 25 mL toluene for 7 days at room temperature. After filtering, the black-gel was dried for 1 day in air at room temperature, and dried in an oven at 70°C until a constant weight was obtained. The percentage of bound rubber content was determined.

Measurement of dynamic mechanical properties

For assessing dynamic mechanical properties, the Rubber Process Analyzer (RPA2000, Alpha Technologies, Akron, OH) was utilized. A strain sweep test was carried out. To determine the dynamic properties of uncured and cured specimens, the test temperatures were of 100 and 40°C, respectively.

Measurement of carbon black dispersion

Morphological observation of the specimen was achieved using a scanning electron microscope (SEM, JEOL model JSM-6301 F). The vulcanized rubber was cryogenically fractured and sputtered with gold to prevent charging on the surfaces before viewing.

RESULTS AND DISCUSSION

Effect of carbon black loading

Uncured rubber compounds

Generally, the processability of unvulcanized compounds could be determined from the Mooney viscosity and Mooney relaxation. The results of Mooney viscosity are shown in Figure 1. It is clear that the Mooney viscosity increases significantly with increasing black loading, which could be explained by the hydrodynamic effect, according to the Guth and Gold equation as illustrated in eq. (1).[21]

$$\eta_{\mathrm{rel}} = \frac{\eta_{\mathrm{f}}}{\eta_{\mathrm{u}}} = 1 + 2.5\phi_{\mathrm{e}} + 14.1\phi_{\mathrm{e}}^2 \qquad (1)$$

where η_{rel}, η_{f}, and η_{u} are the relative Mooney viscosity, and the Mooney viscosity of filled and unfilled compounds, respectively. ϕ_e is the effective filler volume fraction depending strongly on the filler loading

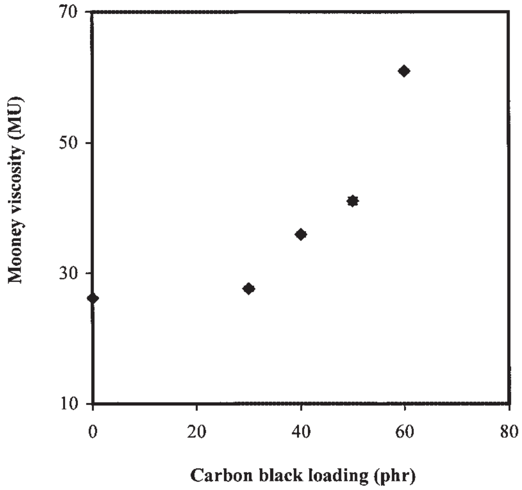
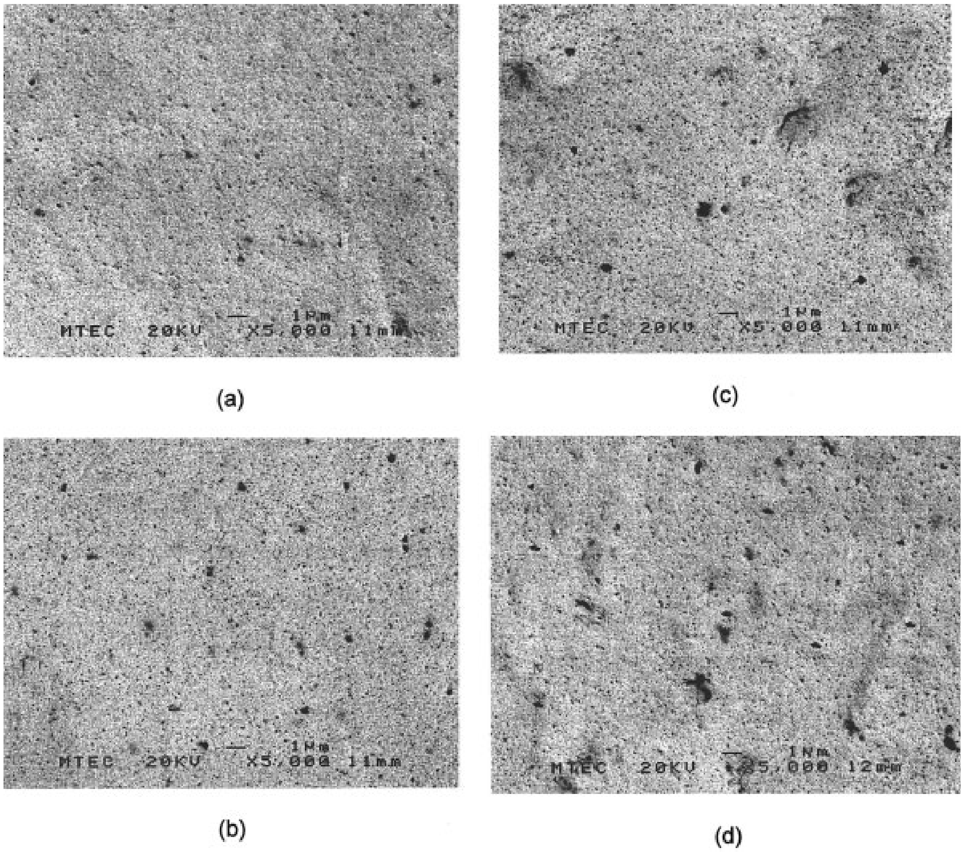


Figure 1 Mooney viscosity of NR compounds as a function of black loadings.



(a) (c)

(b) (d)

Figure 2 Scanning electron micrographs of NR compounds filled with various black loadings: (a) 30 phr; (b) 40 phr; (c) 50 phr; (d) 60 phr.

and the degree of filler dispersion. As shown in previous work,[20,21] the poorer the filler dispersion, the higher the effective filler volume fraction.

Figure 2 reveals that the size of the agglomerate increases as black loading increases, supporting that the increase in Mooney viscosity as a function of black loading is caused mainly by the hydrodynamic effect, as mentioned previously.

In the case of stress relaxation as determined from Mooney relaxation, the SR area and relax 3/1, which are generally defined as the area and slope of the stress relaxation curve, respectively, are used to provide information of a bulk elasticity of test compounds. The high SR area and the low relax 3/1 values indicate the high bulk elasticity. The results obtained, as shown in Table II, reveal an increase in SR area and a decrease in relax 3/1 with increasing black loading. In other words, the bulk elasticity of rubber compounds increases with increasing carbon black loading. The result could be explained by the dilution effect, that is, the amount of the deformable rubber is diluted by the undeformable rigid particles of carbon black.

Dynamic mechanical properties of uncured compounds with various black loading as determined from RPA2000 are shown in Figures 3 and 4. It is evident that there is a region where a storage modulus or elastic modulus (G′) is independent of shear strain or the so-called linear viscoelastic region (LVE) in the unfilled compound. As carbon black is added, the LVE region disappears and G′ at a given shear strain increases as a function of black loading. In addition, the dependence of G′ on shear strain is more pronounced as black loading increases. The result could be explained by the breakdown of the filler-filler transient network (usually known as the Payne effect).[22,23] The rise in G′ as a function of black loading is attributed to the increase in effective filler volume fraction (ϕ_e), known as the hydrodynamic effect. Since the immobilized rubber trapped in the filler network behaves as part of the undeformable fillers, the amount of immobilized rubber is large at high filler content, resulting

TABLE II
Properties of NR Compounds Filled with Different Black Loadings

Carbon black loading (phr)	Mooney characteristics	
	SR area (MU · s)	Relax 3/1
0	85.02 ± 3.18	1.20 ± 0.06
30	428.60 ± 2.26	0.63 ± 0.01
40	702.44 ± 6.00	0.57 ± 0.01
50	841.17 ± 5.23	0.55 ± 0.01
60	1831.09 ± 4.54	0.45 ± 0.01

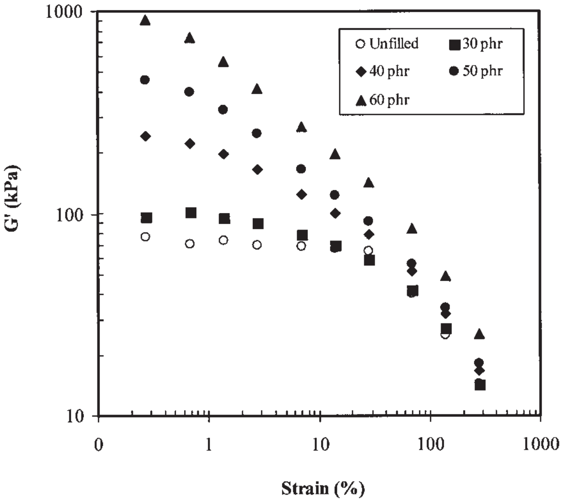


Figure 3 Strain dependence of elastic modulus (G′) at a test frequency of 6.28 rad/s in uncured NR compounds filled with various loadings of black.

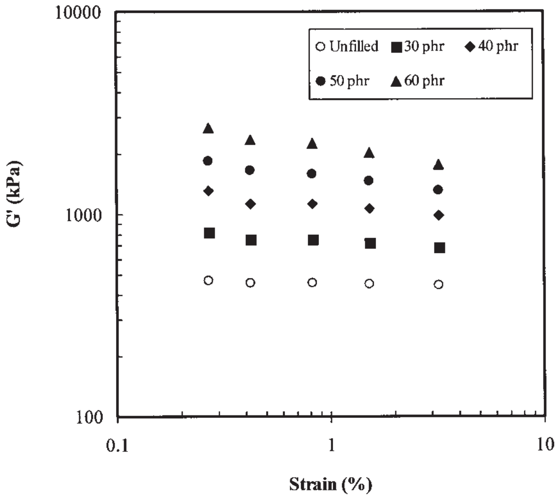


Figure 5 Strain dependence of elastic modulus (G′) at a test frequency of 12.0 rad/s in NR vulcanizates filled with various loadings of carbon black.

in an increase in effective filler volume fraction (ϕ_e), and thus the G′.

The results of the damping factor (tan δ), as shown in Figure 4, reveal an increase in tan δ at high strain amplitude. This is due to the fact that tan δ is dependent on both loss modulus (G″) and storage modulus (G′). It is known that G′ is related to the presence of the filler transient network, which is reduced with increasing dynamic shear strain, while G″ is related to the energy dissipated during the deformation. G″ is generally associated with the breakdown of the filler transient network as well as molecular slippage during deformation, or the so-called hysteretic process. In other words, the increase in tan δ with shear strain is a result of filler network disruption and molecular chain slippage. Notably, at low strain of deformation where the filler transient network still exists, the damping factor slightly decreases with increasing black loading, which could be explained by the dilution effect. As discussed earlier, the high black loading would result in an increase in effective filler volume fraction. In other words, with increasing black loading, the amount of elastomeric phase with viscoelasticity reduces and, thus, the tan δ.

Cured rubber compounds

In the case of NR vulcanizates, Figure 5 shows the LVE region in the unfilled vulcanizate, and the strain-de-

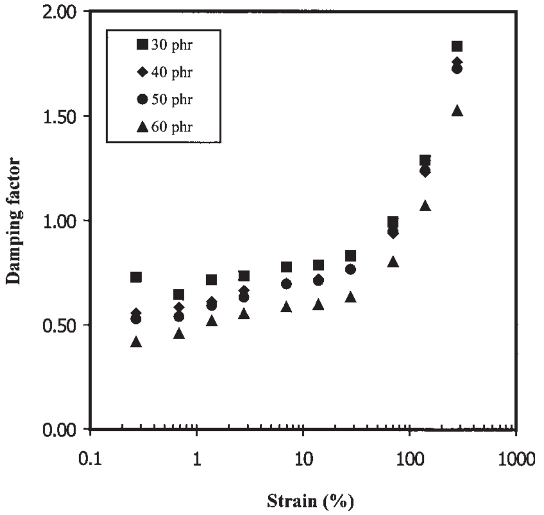


Figure 4 Strain dependence of damping factor (tan δ) at a test frequency of 6.28 rad/s in uncured NR compounds filled with various loadings of black.

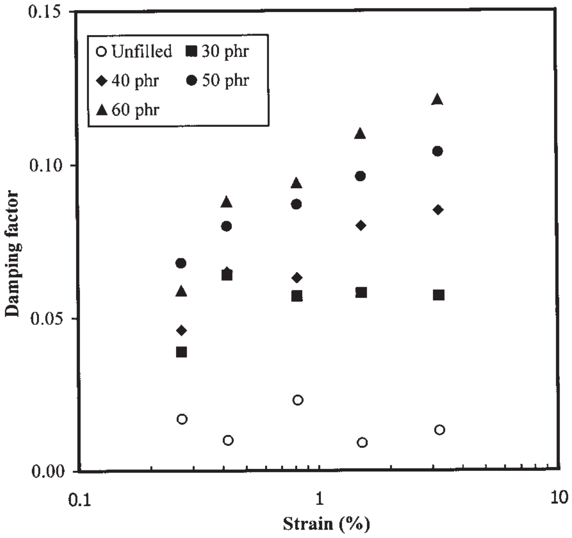


Figure 6 Strain dependence of damping factor (tan δ) at a test frequency of 12.0 rad/s in NR vulcanizates filled with various loadings of carbon black.

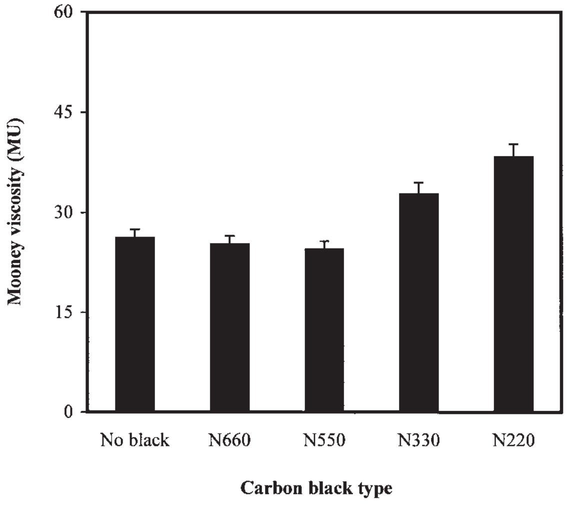


Figure 7 Mooney viscosity of NR compounds filled with various black types.

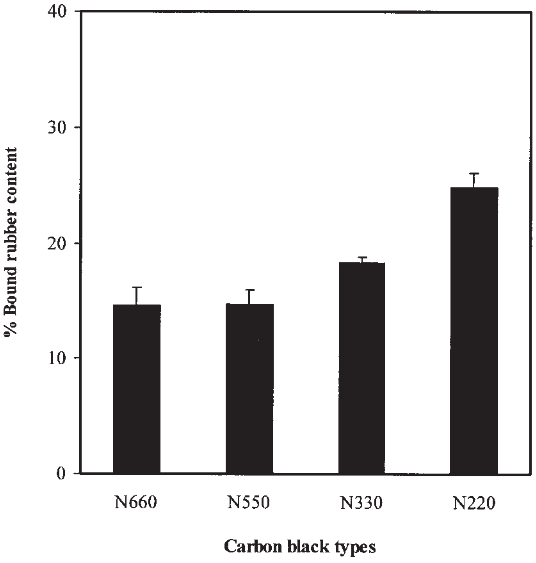


Figure 8 Bound rubber content of NR compounds filled with various black types.

pendent storage modulus in the filled vulcanizates. Compared to uncured compounds, the vulcanizates yield much higher G′, due to the presence of chemically molecular crosslinking. Furthermore, the higher the black loading, the higher the G′, which could again be explained by the hydrodynamic effect.

Unlike the uncured compounds, the tan δ in vulcanizates as illustrated in Figure 6 apparently increases with black loading, which indicates an increase in loss energy for filler network disruption. In other words, the tan δ of vulcanizates is controlled mainly by the disruption and reformation of the filler transient network, rather than the dilution effect found in the case of uncured compounds as discussed previously.

Effect of carbon black type

Uncured rubber compounds

The effect of carbon black type on processability of uncured rubber compounds is illustrated in Figure 7 and Table III. The Mooney viscosity of the compounds appears to increase with increasing specific surface area of carbon black (N220 > N330 > N550 > N660). Similar results are found for the Mooney relaxation, as illustrated in Table III. The explanation for the Mooney result is proposed in terms of an increase in rubber-filler interaction, or bound rubber content, with increasing the specific surface area, as shown in Figure 8. The higher content of bound rubber causes more molecular restriction of the system, that is, a reduction in the Mooney relaxation as observed from an increase in area under the Mooney relaxation curve and a decrease in the relaxation rate (denoted as SR area and relax 3/1, respectively). In addition, one might know that filler dispersion could affect the Mooney viscosity and relaxation, but from the micrographs shown in Figure 9, there is no significant difference in degree of carbon black dispersion in all the compounds. Consequently, the effect of carbon black dispersion on Mooney viscosity and relaxation could be disregarded in the present study.

TABLE III
Properties of NR Compounds Filled with Different Carbon Black Types

	Mooney characteristics	
Carbon black type	SR area (MU · s)	Relax 3/1
Unfilled	50.98 ± 3.18	1.48 ± 0.06
N660	65.42 ± 1.58	1.29 ± 0.02
N550	80.32 ± 2.41	1.21 ± 0.01
N330	157.23 ± 6.31	1.03 ± 0.10
N220	340.43 ± 0.96	0.75 ± 0.00

The influence of the carbon black surface area on dynamic mechanical properties of uncured compounds is shown in Figures 10 and 11. As shown in Figure 10, there is a significant strain-dependent storage modulus (G′) in all uncured filled compounds. At low strain amplitude, the magnitude of the strain-dependent G′ is more obvious as the specific surface area of black increases. The result implies that the amount of filler transient network is larger as the surface of filler increases. Also, the result of tan δ, shown in Figure 11, reveals a decrease in tan δ as the black surface area increases. The result is analogous to that of the filler loading effect as discussed previously. Thus, a similar explanation based on the dilution effect could be applied.

Cured rubber compounds

In the case of the cured compounds, Figure 12 shows a plot of G′ as a function of the shear strain of vulca-

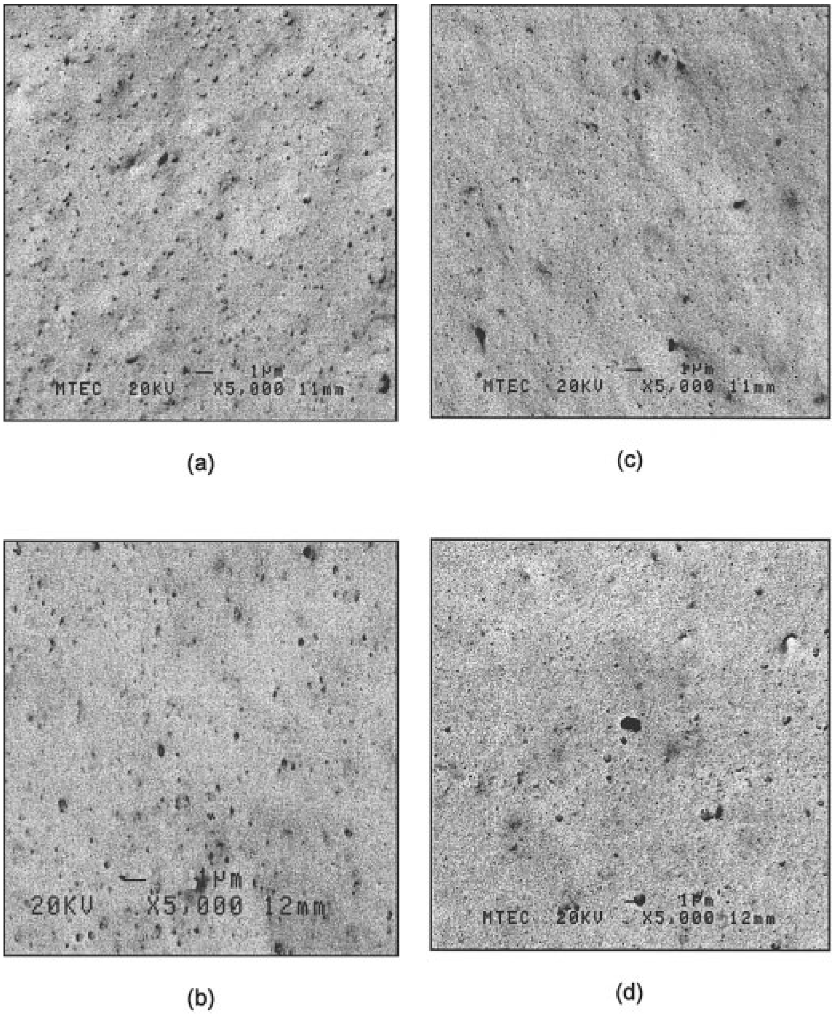


Figure 9 Scanning electron micrographs of NR vulcanizates filled with various carbon black types: (a) N660; (b) N550; (c) N330; (d) N220.

nizates filled with various carbon black surface area. It is clear that G′ increases with increasing specific surface area of carbon black, which could again be ex-

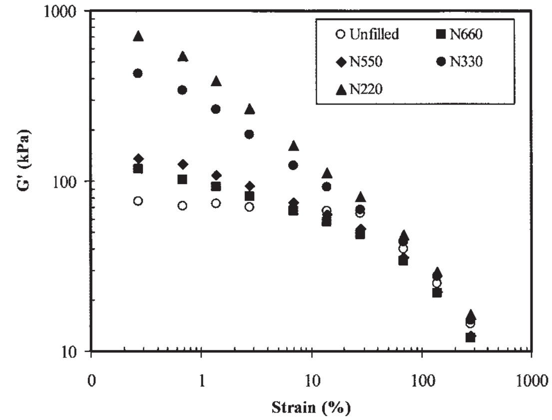


Figure 10 Strain dependence of elastic modulus (G′) at a test frequency of 6.28 rad/s in uncured NR compounds filled with various carbon black types.

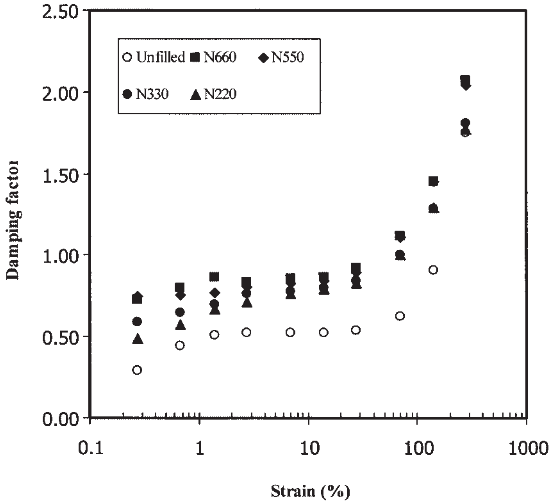


Figure 11 Strain dependence of damping factor (tan δ) at a test frequency of 6.28 rad/s in uncured NR compounds filled with various carbon black types.

plained by the greater polymer-filler interaction effect, according to the result of bound rubber content (see Fig. 8). Figure 13 reveals that tan δ increases as the specific surface area of black increases. This is due to the increase in specific surface areas of carbon black to interact with rubber molecules, leading to an increase in loss modulus and, thus, the tan δ.

CONCLUSIONS

Processability and viscoelastic properties of natural rubber compounds filled with different black loadings and types were investigated with the use of a steady shear rheometer, namely, the Mooney viscometer, and an oscillatory rheometer, namely, the Rubber Process Analyser (RPA2000). The following conclusions could be drawn:

Mooney viscosity and relaxation are influenced strongly by carbon black dispersion and filler-rubber interaction. The higher the black dispersion and/or the stronger the filler-rubber interaction would result in higher Mooney viscosity and bulk elasticity of the rubber compounds.

Type and loading of carbon black strongly influence the dynamic mechanical properties in both uncured and cured NR. Damping factor (tan δ) of the uncured NR decreases with increasing black loading. This is attributed to the reduction of mobilized rubber content in the compound (or the dilution effect). However, in the case of the cured NR, the filler transient network plays a strong role in the vulcanizate damping factor. Therefore, the loss factor increases with increasing black loading and/or with increasing black surface area.

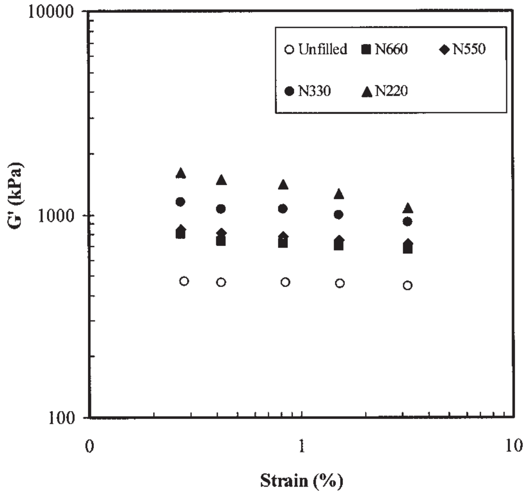


Figure 12 Strain dependence of elastic modulus (G′) at a test frequency of 12.0 rad/s in NR vulcanizates filled with various carbon black types.

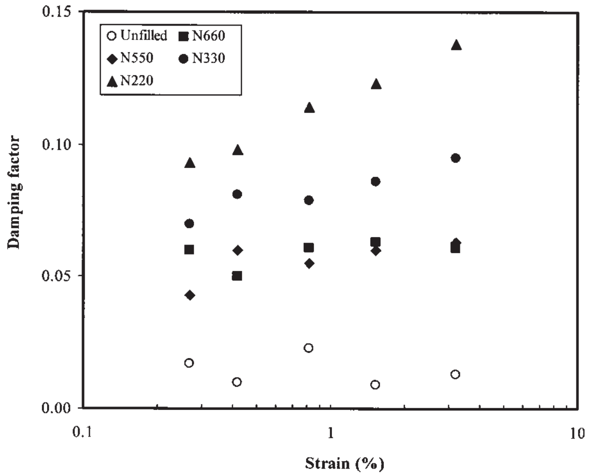


Figure 13 Strain dependence of damping factor (tan δ) at a test frequency of 12.0 rad/s in NR vulcanizates filled with various carbon black types.

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