

Interaction of Vulcanization and Reinforcement of CB on Dynamic Property of NR Characterized by RPA2000

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ABSTRACT: Vulcanization and reinforcement are two most important approaches to improve rubber properties. Effect of carbon black (CB) load level on curing process and properties of Natural rubber (NR) compounds and vulcanizates and interaction between vulcanization and reinforcement were characterized by Rubber Processing Analyzer (RPA2000). The incorporation of CB shortened the scorch delay time and prolonged curing time. Only after CB loading level reached about 20 phr, could effective CB network be formed that contributed to the formation of "Payne effect." Dynamic elastic shear modulus G' of filled NR compounds had a stronger dependence on strain

than that of unfilled NR. There was a synergism between vulcanization and reinforcement on the improvement of shear modulus of NR compounds and vulcanizates. The elastic recovery of vulcanizates restricted the break of CB network through the rubber bridges formed between CB particles and helped the reformation of broken CB network. All these action amplified the reinforcement of CB. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 1168–1172, 2010

Key words: carbon black; reinforcement; vulcanization; synergism; Payne effect

INTRODUCTION

Carbon black (CB) is the most important reinforcing agent for rubber that can improve the mechanical properties of rubber by forming bound rubber between rubber and particle surface of CB.^{1–5} Vulcanization is a process in which linear long chains of rubber molecules become crosslinked through reaction with the vulcanization agents. When CB is incorporated into rubber, CB particles disperse in rubber matrix with the help of mechanical force applied by open mills or internal mixers. But the aggregates still have a tendency to congregate due to their high specific surface area and high surface energy.⁶ So a secondary, physical network can be formed whilst the primary, chemical network is formed by chemical-bonded crosslinks. These two networks coexist in vulcanizates and interact which contributes to the properties of vulcanizates. Numerous works have already shown that the physical work influenced strongly on the load of filler,^{7–9} strain magnitude.^{7,10,11}

Rubber Processing Analyzer RPA2000 is a dynamic rheometer to measure the dynamic proper-

ties in a certain range of frequency, temperature, and strain for polymers before and after curing.¹² Dual effect of vulcanization and reinforcement on viscoelasticity of Natural Rubber (NR) compounds and vulcanizates will be studied using RPA2000 in this article.

EXPERIMENTAL

Sample preparation

The raw NR was masticated first on a two-roll mill by passing through the nip till a smooth band is formed on the front roll. After that, zinc oxide, stearic acid, and accelerator were added and mixed for 2 min with a rolling bank and 3 cuts on each side. Then, CB was added and mixed for 3 min and 4 cuts on each side. Finally, sulfur was added and mixed for 2 min and 3 cuts. Five additional passes were made and then the compound was slabbed and stored at room temperature for at least 8 h. Isothermal vulcanization was performed using RPA20000.

Formulation of the compound

The compound formulations of different CB loading levels are shown in Table I. The concentration of all compound ingredients used is normally given based on a total of 100 parts of NR rubber by weight.

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TABLE I
Compound Formulation of Different CB Load

Ingredient	CB-0	CB-10	CB-20	CB-30	CB-50
Natural rubber (NR)	100	100	100	100	100
Zinc oxide	5	5	5	5	5
Stearic acid	2	2	2	2	2
Accelerator TBBS ^a	1	1	1	1	1
N330	0	10	20	30	50
Sulfur	2.5	2.5	2.5	2.5	2.5

^a TBBS: *N-t*-butylbenzothiazole-2-sulfenamide.

Measurement on RPA2000

Curing was performed on RPA2000 at the temperature of 145°C, frequency of 100 cpm, and strain amplitude of 0.2°. For strain sweep, the temperature was 60°C, the frequency was 60 cpm, and the strain was between 0.1 and 100%.

RESULTS AND DISCUSSION

Curing characteristic of NR with different CB load

NR with different CB load (0, 10, 30, and 50 phr) was cured in RPA 2000 at 145°C. The cure curves and cure

characteristics such as scorch delay time (t_{s1}), optimum curing time (t_{90}), and theoretical curing time (t_H) were shown in Figure 1 and Table II, respectively.

It could be seen from Table II that the incorporation of CB shortened the scorch delay time from 5.18 min for unfilled NR to 2.89 min for NR with 50 parts CB, whereas the optimum curing time was prolonged from 9.85 min to 10.27 min. The higher the CB load, the shorter the scorch delay time was.

The development of elastic torque (S') is usually used to characterize the cure state of rubber which is based on the assumption that the modulus of rubber under shear stress is proportional to the concentration of crosslink in vulcanizate. In fact, more elaborate structural change during curing process can be observed from the evolution of viscous torque (S'') as shown in Figure 1.

Before there was an apparent increase in elastic torque S' in cure-curve which was usually related to the formation of crosslink, an increase of viscous torque S'' occurred apparently, indicating crosslink reactions between several rubber molecules had already begun which led to the formation of local primary network by one or more crosslinks. This kind of crosslink was similar to rubber molecules with

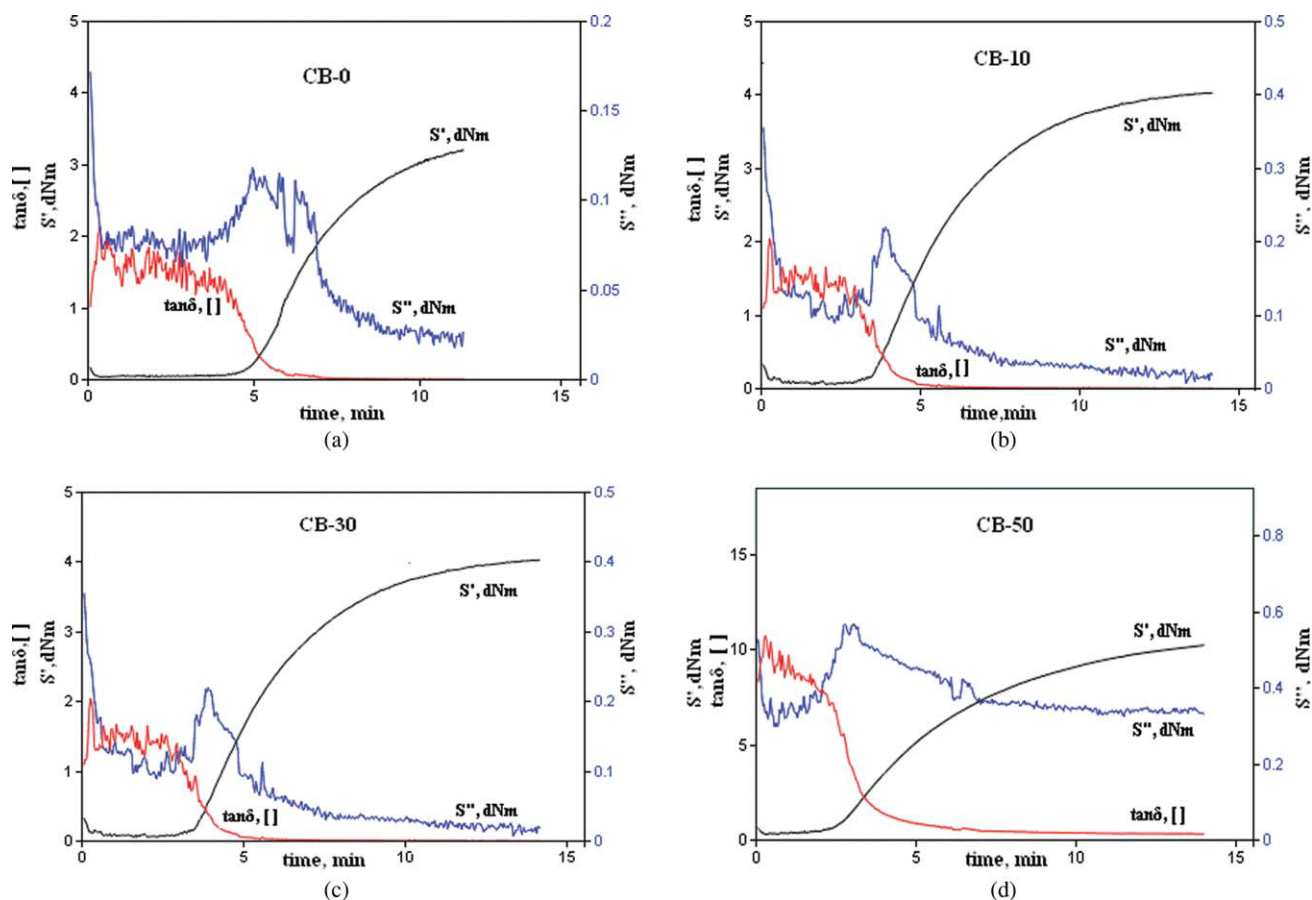


Figure 1 Cure curves of NR with different CB loads (a) 0 phr CB; (b) 10 phr CB; (c) 30 phr CB; (d) 50 phr CB. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Cure Characteristic of NR with Different CB Loading

Samples	t_{10}/min	t_{90}/min	t_H/min
CB-0	5.18	9.85	11.35
CB-10	3.82	9.51	13.20
CB-20	3.79	9.36	13.51
CB-30	3.75	9.21	13.72
CB-50	3.27	9.01	14.00

long branches. The formed network is not strong enough to bear the force exerted by the moving die and there was relative slide between rubber molecules under force, so S' was not high enough to be observed. With the further going of cure time, both elastic and viscous torques went up due to the formation of more crosslinks. S'' reached its maximum value when S' increased to only about 10% of its maximum value S'_{\max} . S' still kept going up, whereas S'' decreased dramatically. This point might be taken as the "gel point"¹³ of crosslinking reaction at which an almost complete network had been formed and the rubber transformed from a viscous state to an elastic one. After that point, the crosslink points became denser and denser, making S'' and $\tan \delta$ lower and lower. The crosslinking reaction came to the end till both torque (S' , S'') and hysteresis loss factor $\tan \delta$ became leveled of.

Table III showed the elastic, viscous shear torque S' , S'' , $\tan \delta$ at minimum and maximum torques. The incorporation of CB increased the torques of both NR compound and vulcanizate. It could be seen apparently that there was a synergistic effect between the reinforcement of CB and crosslinking on elastic torque. For example, before vulcanization, 50 parts CB increased the elastic torque of NR compounds by 0.27 dN m, and the vulcanization increased the elastic torque of NR gum 3.16 dN m, but 50 parts CB increased the elastic torque of NR vulcanizates by 7.05 dN m, much higher than the sum of the contribution of vulcanization and reinforcement, 3.43 dN m.

Influence of CB load on dynamic elastic modulus of NR compounds

CB-filled rubber is known as a kind of nonlinear viscoelastic material which means the dynamic prop-

TABLE III
Comparison of S' , S'' , and $\tan \delta$ of NR with Different CB Load

Samples	$S'_{\min}/\text{dN m}$	$S'_{\max}/\text{dN m}$	$(S'_{\max} - S'_{\min})/\text{dN m}$	$\tan \delta$ at S'_{\min}	$\tan \delta$ at S'_{\max}
CB-0	0.04	3.20	3.16	2.031	0.006
CB-10	0.06	4.04	3.98	1.573	0.005
CB-30	0.15	6.37	6.22	1.338	0.016
CB-50	0.31	10.25	9.94	1.077	0.033

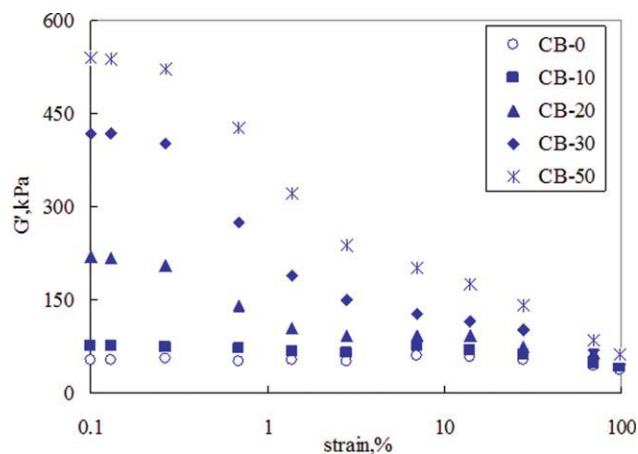


Figure 2 Dependence of G' on strain of NR compounds with different CB loads. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

erties of CB-filled rubber has a dependence on dynamic strain amplitude. This kind of strain-amplitude dependence is also called Payne effect, that is, at a set frequency and temperature, the elastic modulus (G') of a filled rubber will decrease from a high plateau value G'_0 at a lower strain amplitude to a low plateau value G'_∞ at a higher strain amplitude.

Figure 2 showed the dependence of G' on strain of NR compounds with different CB load at 60°C and a shear frequency of 60 cpm.

It was seen that, for unfilled NR compound and compound with lower CB load (CB load less more than 20 parts), no Payne effect was observed. The elastic modulus G' almost kept constant and only showed a slight decrease when the strain exceeded 63%. As CB load exceeded 20 parts (including 20 parts), apparent Payne effect was observed. The G' decreased dramatically at strain 0.26%, and G'_∞ almost reached the same value as that of unfilled rubber at the ultimate strain of 100%.

The decrease of G' was explained by the breakage of physical bonds between fillers, more accurately, the breakage of three-dimensional network formed by CB aggregates and agglomerates. Because of their high specific surface area and high surface energy, CB particles have a high tendency to congregate after having been dispersed in rubber matrix through strong mechanical force. For compound with low CB load, the CB particles were dispersed in the rubber matrix and the distances between carbon particles were so far that they could not connect with each other, so no Payne effect was observed. When the CB load was high enough (here not less than 20 parts), a rigid three-dimensional network was formed which contributed a lot to the modulus of NR compounds. At lower strain, the filler network could not be fractured, and the higher the CB load,

the more the network was formed, and the higher was the modulus. With the increase of strain amplitude, the rigid network became fractured that initiated the sharp decrease of modulus. When strain was high enough, the whole CB network was destroyed and the modulus of compounds (G'_{∞}) decreased to almost the same level which was only contributed by rubber matrix.

Influence of CB load on dynamic property of NR vulcanizates

Figure 3 showed the dependence of G' on strain of cured NR with different CB load at 60°C and a shear frequency of 60 cpm.

Similar Payne effect to that of NR compounds was observed in NR vulcanizates when CB load was higher than 20 parts and the cured NR had much higher elastic modulus G' than that of uncured NR with the same ingredients and CB load because of the introduction of chemically bonded crosslinks.

$(G'_0 - G'_{\infty})$ is usually used to characterize the contribution of CB network to elastic modulus. Figure 4 showed the comparison of $(G'_0 - G'_{\infty})$ for NR before and after cure.

It was seen that, for uncured NR compound, $(G'_0 - G'_{\infty})$ increased almost linearly with the increase of CB load. NR vulcanizate with the same CB load had higher $(G'_0 - G'_{\infty})$ values than that of uncured rubber. The reason may be that more rubber chains were attached to the surface of CB during vulcanization, the reinforcement of CB is hence intensified, so the $(G'_0 - G'_{\infty})$ of vulcanizates were much higher than those of compounds, especially for NR with higher CB load level, indicating a synergistic effect between vulcanization and reinforcement of CB on elastic modulus.

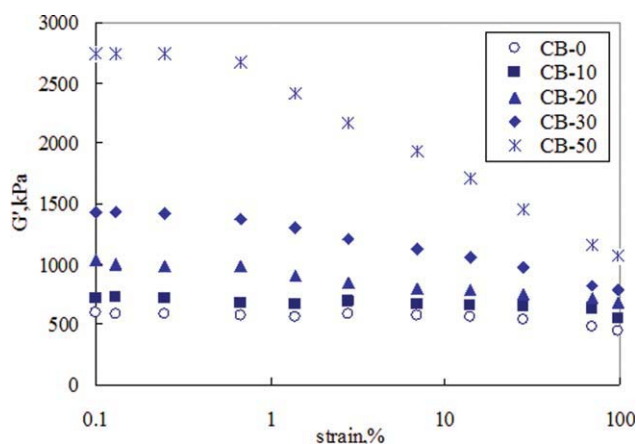


Figure 3 Dependence of G' on strain of NR vulcanizates with different CB loads. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

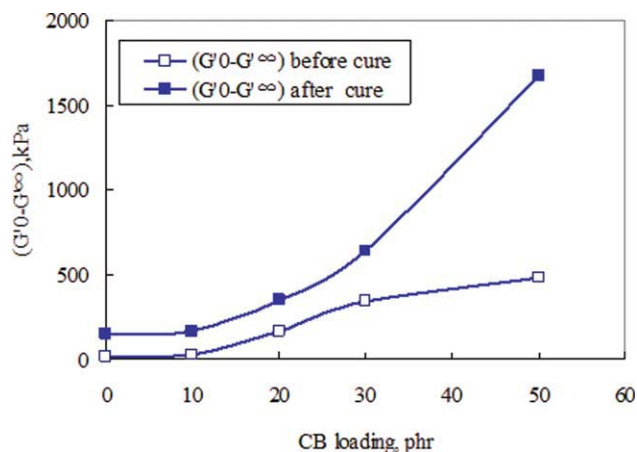


Figure 4 Comparison of $(G'_0 - G'_{\infty})$ for NR compounds and vulcanizates. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 5 also showed comparison of ultimate elastic modulus at high strain (G'_{∞}) for uncured and cured NR.

Figure 5 indicated that, unlike uncured NR which had almost similar G'_{∞} at large strain, cured NR with the same CB load had a higher elastic modulus value (G'_{∞}) than uncured NR and the value of G'_{∞} increased as CB load increased. This is because CB particles dispersed in different media before and after vulcanization and this changed some characteristics of CB network. In fact, the characteristic of rubber has an influence on the dispersion of CB, and the amount and size of CB agglomerates. The CB network is formed not only through direct contacting of adjacent CB aggregates, the rubber chains adsorbed on the surface of CB particles (bound rubber layer) can also form soft filler network through flexible contacting as shown in Figure 6.

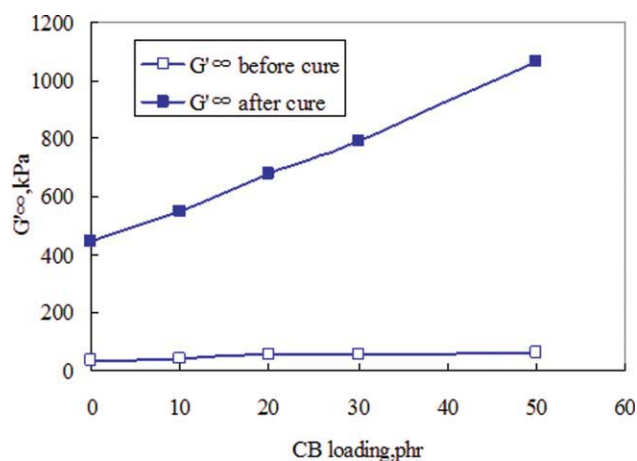


Figure 5 Comparison of G'_{∞} for NR compounds and NR vulcanizates. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

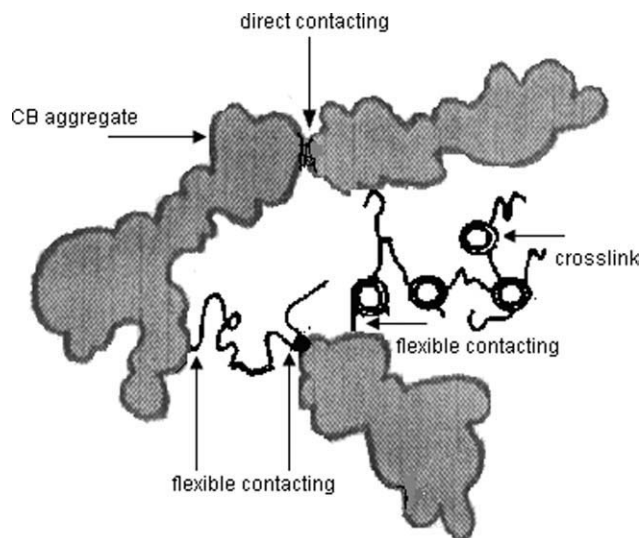


Figure 6 Schematic of rigid and flexible contacting of CB network in NR vulcanizates.

The development of filler network under dynamic strain is a balance between breaking and rejoining of rigid and flexible contacting points.¹⁴ After vulcanization, the recovery of rubber chains with high elasticity became quickly and forcibly that led to the rejoining of CB particles by flexible contacting easily. The result of easy-rejoining led to much higher G'_{∞} of NR vulcanizates than those of NR compounds as shown in Figure 5.

CONCLUSIONS

1. The incorporation of CB shortened scorch delay time and prolonged the curing time of NR.

2. Only when CB loading level reached about 20 phr, could effective CB network of CB aggregates be formed that resulted in "Payne effect." Dynamic elastic shear modulus G' of filled NR compounds had a stronger dependence on strain than that of unfilled NR.
3. There was a synergistic effect between vulcanization and reinforcement in which the elastic recovery of rubber chains in vulcanizates amplified the reinforcement of CB by restricting the break of CB network through the rubber bridges formed between CB particles and helping the reformation of broken CB network.

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