

# Effect of Bound Rubber on Characteristics of Highly Filled Styrene–Butadiene Rubber Compounds with Different Types of Carbon Black

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**ABSTRACT:** Viscosity and cure time of a filled rubber compound having an accelerated sulfur cure system are affected by types and contents of the rubber and the filler as well as of the curatives. Bound rubber content is used as level of the reinforcement. Influence of bound rubber on viscosity and cure time of a rubber compound was studied using highly filled styrene–butadiene rubber compounds with carbon black having different structures. The bound rubber content increases with increase of the carbon black content and also increases as the carbon black structure is

developed. The Mooney viscosity increases linearly with increase of the bound rubber content irrespective of the carbon black structure when the primary particle size of carbon black is nearly the same. The Mooney scorch time decreases linearly with increase of the bound rubber content irrespective of the carbon black structure. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1001–1006, 2004

**Key words:** bound rubber; viscosity; cure time; filled rubber compound

## INTRODUCTION

Factors affecting the cure characteristics of filled rubber compounds having an accelerated sulfur cure system are very complicated. Content of sulfur is critical. The more the sulfur content, the faster the cure time and the higher the crosslink density. In general, cure accelerators make the crosslinking reactions fast and the crosslink density high. Types and contents of cure accelerators and sulfur content determine the cure characteristics such as scorch time, cure rate, optimum cure time, and crosslink density.<sup>1–6</sup> Rubbers have different cure characteristics according to their chemical properties.<sup>7,8</sup> Styrene–butadiene rubber (SBR) has slower cure characteristics than natural rubber (NR) or butadiene rubber (BR) but the former has a better reversion resistance than the latter.

Types and contents of fillers also affect the cure characteristics.<sup>9–12</sup> Silica-filled rubber compounds have slower cure characteristics than carbon black-filled ones since silica adsorbs curatives.<sup>13–16</sup> The crosslink density is also influenced by the structure and surface chemistry of carbon black.<sup>9,10</sup> Cure rate of a filled rubber compound is faster than that of an unfilled one.<sup>10,11</sup> Carbon black increases the crosslink density and improves the reversion resistance.<sup>10,17</sup>

Bound rubber phenomenon and its effect on properties of filled rubber compounds and vulcanizates have been studied.<sup>18–22</sup> The bound rubber depends on characteristics of filler such as surface area, structure or morphology, and surface activity. With regard to the polymer, the chemical structure (saturated or unsaturated and polar or nonpolar) and the microstructure (configuration, molecular weight, and molecular weight distribution) influence the level of bound rubber content.

Bound rubber is an important factor in reinforcement. Bound rubber is a parameter that is simple to measure but the factors that influence the test results are very complicated. The filler–polymer interaction leading to the formation of bound rubber involves physical adsorption, chemisorption, and mechanical interaction. Moreover, bound rubber also shows a dependence on the processing conditions of the compound, such as mixing and storage times.<sup>22–26</sup> In general, bound rubber content is measured by extracting the unbound rubber with solvent. Factors affecting the bound rubber content during the measurement are the nature of the solvent and the temperature of extraction.

In the present work, influence of bound rubber on viscosity and cure time of a rubber compound was studied using highly filled styrene–butadiene rubber compounds with carbon blacks. To investigate the influence of carbon black structure on the cure characteristics, three type carbon blacks with similar pri-

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TABLE I  
Formulations (phr)

Compound no.	1	2	3	4	5	6	7	8	9	10	11	12
SBR 1500	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
N326	80.0	90.0	100.0	110.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N330	0.0	0.0	0.0	0.0	80.0	90.0	100.0	110.0	0.0	0.0	0.0	0.0
N351	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	80.0	90.0	100.0	110.0
ZnO	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
HPPD	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Wax	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
TBBS	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
Sulfur	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2

SBR 1500: styrene-butadiene rubber with styrene content of 23.5 wt%.

HPPD: *N*-phenyl-*N'*-(1,3-dimethylbutyl)-*p*-phenylenediamine.

TBBS: *N*-*tert*-butyl-2-benzothiazole sulfenamide.

mary particles but different structures were employed.

### EXPERIMENTAL

The carbon black-filled styrene-butadiene rubber (SBR) compounds were made of SBR, carbon black, cure activators (stearic acid and ZnO), antidegradants (HPPD and wax), and curatives (TBBS and sulfur). The filler contents were 80.0, 90.0, 100.0, and 110.0 phr. N326, N330, and N351, having similar primary particles but different structures, were employed as carbon blacks. The dibutylphthalate (DBP) absorption values are 71.4, 99.7, and 107.0 mL/100 g for N326, N330, and N351, respectively. In general, DBP value is used as the degree of filler structure. The formulations are given in Table I.

Mixing was performed in a Banbury type mixer at a rotor speed of 40 and 25 rpm for master batch (MB) and final mixing (FM) stages, respectively. The initial temperatures of the mixer were 110 and 80°C for MB and FM stages, respectively. The MB compounds were prepared as follows. (1) The rubber was loaded into the mixer and preheated for 0.5 min. (2) The carbon black of 50.0 phr was compounded into the rubber for 1.0 min. (3) The rest carbon black and the ingredients were mixed for 2.5 min and the compounds were discharged. The FM compounds were prepared by mixing the curatives with the MB compounds for 2.0 min.

Mooney tests to measure viscosity and cure times of the compounds were performed with a Mooney viscometer MV 2000 of Alpha Technologies (USA). The small rotor was used because the viscosities of compounds are too high. The test temperatures for measurement of viscosity and cure times were 120 and 135°C, respectively. The preheating time was 1 min. Contents of bound rubber were determined by extracting the unbound materials such as ingredients and free rubbers with toluene for 7 days at room temperature or at

90°C and *n*-hexane for 1 day and drying for 2 days at room temperature. Weights of the samples before and after the extraction were measured and the bound rubber contents were calculated as (Equation 1).

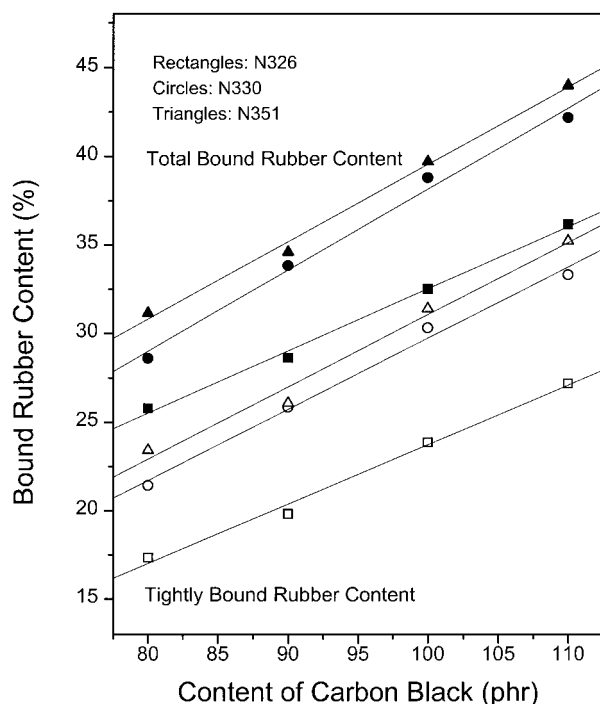
$$R_b(\%) = 100 \times [W_{fg} - W_t[m_f/(m_f + m_r)]] / W_t[m_r/(m_f + m_r)] \quad (1)$$

where  $R_b$  is the bound rubber content,  $W_{fg}$  the weight of filler and gel,  $W_t$  the weight of the sample,  $m_f$  the fraction of the filler in the compound, and  $m_r$  the fraction of the rubber in the compound.

### RESULTS AND DISCUSSION

Bound rubber contents were measured at room temperature and 90°C. Bound rubber is composed of loosely and tightly bound ones.<sup>27,28</sup> The loosely bound rubber exists in an outer shell around the filler while the tightly bound rubber is in the immediate vicinity of the filler particle. The tightly bound rubber is much less mobile than the loosely bound rubber.<sup>28-30</sup> In general, measurement of the bound rubber content is performed under the restricted condition at low temperature (near room temperature) and under the static condition, to prevent the bound rubber (especially the loosely bound one) from extracting. If the extracting temperature is high or the vessel containing the sample and solvent is shaken, some loosely bound rubber will be extracted. The loosely bound rubber can be extracted by the solvent at high temperature since binding energy of the loosely bound rubber is low. Bound rubber content is decreased as the extraction temperature becomes higher.<sup>31</sup> In this study, the tightly bound rubber was obtained by extracting the unbound and loosely bound rubbers at high temperature of 90°C.

Figure 1 shows variations of total and tightly bound rubber contents with the content of carbon black.



**Figure 1** Variation of the bound rubber contents with the carbon black content. Rectangles, circles, and triangles indicate the N326, N330, and N351, respectively. The solid and open symbols stand for the total and tightly bound rubber contents, respectively.

Bound rubber contents measured at room temperature and 90°C were used as total and tightly bound rubber contents. The bound rubber contents increase linearly with increasing the carbon black content, irrespective of the carbon black type. The increased ratios of total bound rubber content are about 3.5, 4.6, and 4.4% per 10 phr for the compounds filled with N326, N330, and N351, respectively. For the tightly bound rubber contents, the increased ratios are about 3.4, 4.0, and 4.1% per 10 phr, respectively. The bound rubber contents have an order of N351 > N330 > N326. This is correspondent with the order of degree of the carbon black structure (DBP absorption value) of N351 > N330 > N326. This implies that formation of bound rubber is very closely related with the filler structure.

Carbon black particle size is the primary property that determines the fineness or surface area. Particle sizes of N326, N330, and N351 are nearly the same.<sup>32</sup> Carbon black aggregate size and structure are determined by the particle size and the number of particles per aggregate. The term "structure" refers to the degree of clustering of the particles within an aggregate, with low structure aggregates being compact in nature and high structure aggregates containing branches with void space between the branches.<sup>32</sup> The total amount of void space can be measured through the absorption of *n*-dibutyl phthalate oil (ASTM D 2414-93). Bound rubber content in carbon black-filled rubber compounds increases with increasing

the surface area of carbon black.<sup>24</sup> The bound rubber contents have an order of N351 > N330 > N326. However, there is no big difference in the surface areas of N326, N330, and N351 (84, 83, and 73 m<sup>2</sup>/g, respectively), and moreover, the surface area has a reverse order of N326 > N330 > N351. Thus, the filler structure (DBP value) is concluded to be the factor responsible for bound rubber formation.

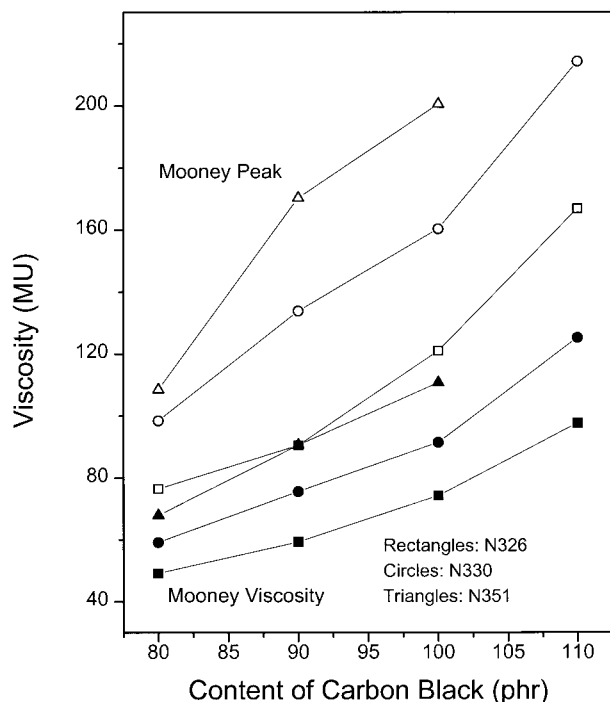
Of the total bound rubber content, ratio of the tightly bound rubber content is 67–80% (Table II). The ratio of tightly bound rubber content (%) is 100 × (tightly bound rubber content / total bound rubber content). The ratio of tightly bound rubber content increases with increasing the carbon black content. The ratio of tightly bound rubber content has an order of N351 > N330 > N326. This implies that the tightly bound rubber is formed better and better as the filler structure is developed more and more.

Figure 2 shows the variation of the Mooney viscosity and Mooney peak as a function of the carbon black content. The Mooney peak is the initial viscosity after the preheating. In general, Mooney viscosity is measured at 100°C using the large rotor when a sample is not too viscous. In this study, the measurement temperature was 120°C and the small rotor was used since viscosities of the compounds were too high. The Mooney viscosity and Mooney peak increase with increasing of the carbon black content. This is due to the increased bound rubber content. The Mooney viscosity and Mooney peak also have an order of N351 > N330 > N326. This is also explained with the increased bound rubber content. Leblanc reported the increased Mooney viscosity and Mooney peak with increase of the bound rubber content.<sup>27</sup>

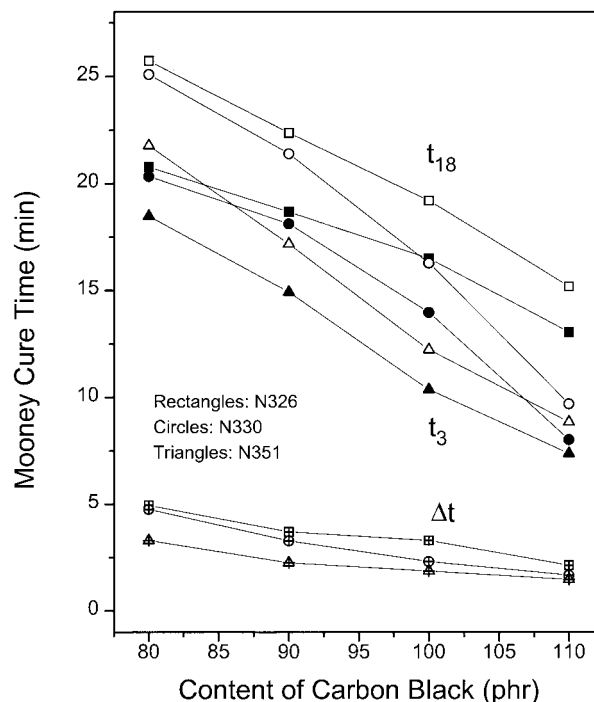
Figure 3 shows the variation of the Mooney cure times as a function of the carbon black content. In general, Mooney cure times are measured at 125°C using the large rotor when a sample is not too viscous. In this study, the measurement temperature was 135°C and the small rotor was used since viscosities of the compounds were too high. The  $t_3$  and  $t_{18}$  means the times taken for the viscosity to reach from the minimum point to increases of 3 and 18 MU, respectively. The  $\Delta t$  ( $= t_{18} - t_3$ ) is used as the cure rate index. The  $t_3$ ,  $t_{18}$ , and  $\Delta t$  decrease with increase of the carbon black content. This means that the scorch time and the

**TABLE II**  
Ratios of Tightly Bound Rubber Content of Total Bound Rubber Content (%)

Carbon black content (phr)	80	90	100	110
N326	67.26	69.22	73.42	75.17
N330	74.90	76.41	78.14	78.95
N351	75.18	75.37	79.06	80.04



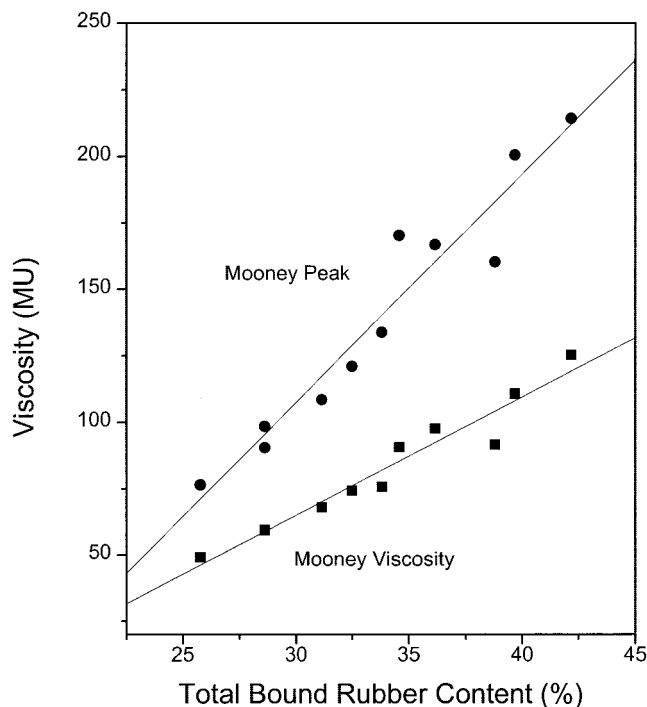
**Figure 2** Variation of the Mooney viscosity and Mooney peak (MS 1 + 4 at 120°C) with the carbon black content. Rectangles, circles, and triangles indicate the N326, N330, and N351, respectively. The solid and open symbols stand for the Mooney viscosity and Mooney peak, respectively.



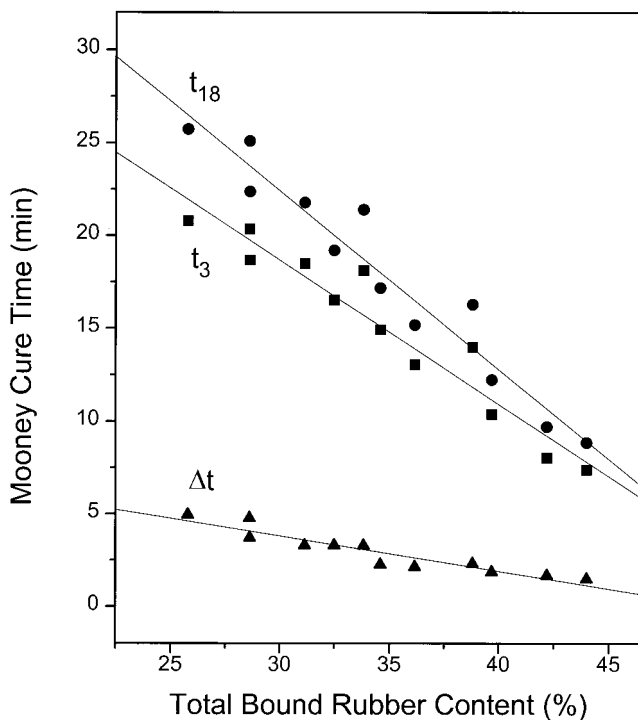
**Figure 3** Variation of the Mooney cure times at 135°C with the carbon black content. Rectangles, circles, and triangles indicate the N326, N330, and N351, respectively. The solid, open, and crossed symbols stand for the  $t_3$ ,  $t_{18}$ , and  $\Delta t$ , respectively.

cure rate become faster as the bound rubber content increases. Cure times depend on contents of sulfur and cure accelerator. The more the contents of sulfur and cure accelerator, the faster the scorch time and cure rate. Thus, the experimental results (Fig. 3) suggest that the increased bound rubber content has an effect of the increased curatives in the compound. This implies that curative concentration in the bound rubber phase is much lower than that in the unbound rubber one. It is hard for the curatives to move through the bound rubber phase since the tightly bound rubber exists in the immediate vicinity of the filler. The compounds containing N351 have shorter cure times and higher cure rates than the compounds containing N326 or N330. The cure times of the compounds containing N330 are shorter than those of the compounds containing N326. This is due to the bound rubber content. The bound rubber content has an order of N351 > N330 > N326 as discussed previously.

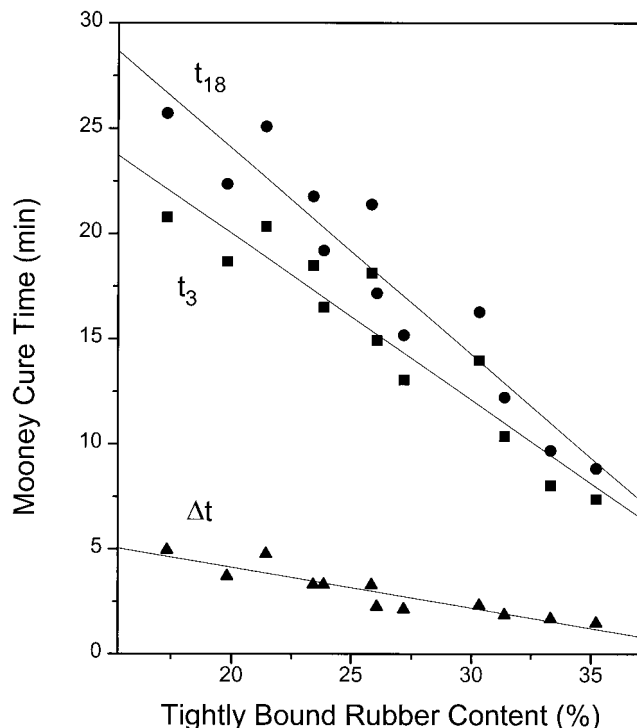
Figures 4-7 give the combined results for the compounds containing different carbon blacks of N326, N330, and N351. Figure 4 shows the variation of the Mooney viscosity and Mooney peak as a function of the total bound rubber content. The Mooney viscosity and Mooney peak increase linearly with increase in the bound rubber content and they have good linear correlations. The correlation coefficients are 0.97 and 0.96 for the Mooney viscosity and Mooney peak, re-



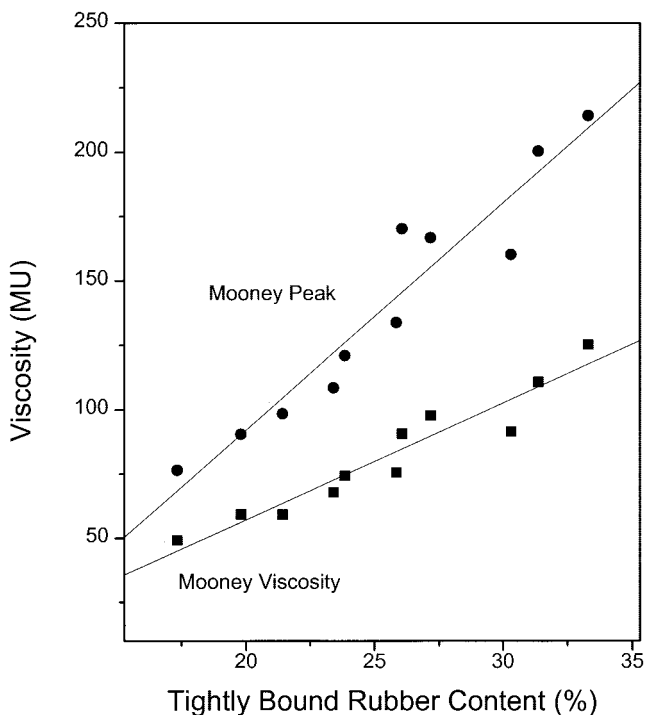
**Figure 4** Variation of the Mooney viscosity and Mooney peak (MS 1 + 4 at 120°C) with the total bound rubber content. Rectangles and circles indicate the Mooney viscosity and Mooney peak, respectively.



**Figure 5** Variation of the Mooney cure times at 135°C with the total bound rubber content. Rectangles, circles, and triangles indicate the  $t_3$ ,  $t_{18}$ , and  $\Delta t$ , respectively.



**Figure 7** Variation of the Mooney cure times at 135°C with the tightly bound rubber content. Rectangles, circles, and triangles indicate the  $t_3$ ,  $t_{18}$ , and  $\Delta t$ , respectively.



**Figure 6** Variation of the Mooney viscosity and Mooney peak (MS 1 + 4 at 120°C) with the tightly bound rubber content. Rectangles and circles indicate the Mooney viscosity and Mooney peak, respectively.

spectively. This implies that the Mooney viscosity and Mooney peak increase linearly with increasing the total bound rubber content irrespective of the carbon black type when the primary particle size is nearly the same. The Mooney viscosity and Mooney peak increase about 4.45 and 8.58 MU per 1% of the total bound rubber content. The increased Mooney peak is about twice the increased Mooney viscosity.

Figure 5 shows the variation of the  $t_3$ ,  $t_{18}$ , and  $\Delta t$  as a function of the total bound rubber content. The  $t_3$ ,  $t_{18}$ , and  $\Delta t$  also have a linear correlation with the total bound rubber content. The correlation coefficients are  $-0.96$ ,  $-0.97$ , and  $-0.94$  for the  $t_3$ ,  $t_{18}$ , and  $\Delta t$ , respectively. This implies that the  $t_3$ ,  $t_{18}$ , and  $\Delta t$  become shorter linearly with an increase in the total bound rubber content, irrespective of the carbon black type, when the primary particle size is nearly the same. The  $t_3$ ,  $t_{18}$ , and  $\Delta t$  decrease about 0.776, 0.963, and 0.191 min per 1% of the total bound rubber content.

Figures 6 and 7 give the combined results as a function of the tightly bound rubber content. The  $t_3$ ,  $t_{18}$ , and  $\Delta t$  as well as the Mooney viscosity and Mooney peak have a linear correlation with the tightly bound rubber content. The correlation coefficients for the Mooney viscosity and Mooney peak are both 0.96. This implies that the Mooney viscosity and Mooney peak increase linearly with increasing the tightly bound rubber content, irrespective of the carbon black type, when the primary particle size is nearly the



same. The Mooney viscosity and Mooney peak increase about 4.55 and 8.83 MU per 1% of the tightly bound rubber content. This is slightly higher than for the total bound rubber content. It implies that the tightly bound rubber content affects the viscosity more strongly than the total bound one.

The correlation coefficients for the  $t_3$ ,  $t_{18}$ , and  $\Delta t$  are  $-0.95$ ,  $-0.95$ , and  $-0.92$ , respectively (Fig. 7). This implies that the  $t_3$ ,  $t_{18}$ , and  $\Delta t$  become faster linearly with increase in the tightly bound rubber content, irrespective of the carbon black type, when the primary particle size is nearly the same. The  $t_3$ ,  $t_{18}$ , and  $\Delta t$  decrease about 0.792, 0.9682, and 0.194 min per 1% of the tightly bound rubber content. This is also higher than for the total bound rubber content. It can lead to a conclusion that the tightly bound rubber content affects the cure times more strongly than the total bound one.

### CONCLUSION

The total and tightly bound rubber contents increase with increase in the carbon black content and the level increases as the filler structure is developed (DBP absorption value increases). The viscosity increases and the cure times become faster with an increase in the carbon black content. This is due to the increased bound rubber content. When the carbon blacks have the same primary particle size but have different structures, the increased viscosity and fast cure times with the carbon black content are explained by the increased bound rubber content, irrespective of the filler type. The tightly bound rubber is found to be more effective to increase the viscosity and to make the cure times fast than the total bound rubber.

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