Influence of Solvent Swell and Bound Rubber on Wax Solubility of Carbon Black-Reinforced NR Composite

Sung-Seen Choi,[1] Song-Hee Im,[1] Changwoon Nah[2]

[1]Department of Chemistry, Sejong University, Gwangjin-gu, Seoul 143-747, Korea
[2]WCU Energy Harvesting Research Team, Department of Polymer-Nano Science and Technology, Chonbuk National University, Jeonju 561-756, Korea

ABSTRACT: Wax in a rubber article migrates to the surface and plays the role of an antidegradant by formation of an impervious barrier on the surface. Wax solubility of a rubber article is important for understanding migration behaviors and film formation of wax as well as for determining the proper content of wax in a rubber compound. Wax solubilities of natural rubber composites reinforced with carbon black were measured using wax solution in toluene. A variation of the wax solubility with the carbon black content was investigated. Raw wax solubility decreased with the increase of carbon black content. Solvent swell-corrected wax solubility also decreased with the carbon black content. The raw wax solubilities were corrected with the rubber fractions, total bound rubber contents, and tightly bound rubber contents as well as the solvent swelling ratio to investigate the influencing parameters on wax solubility. It was found that the unbound and loosely bound rubber fractions as well as the solvent swelling enhanced the wax solubility while the tightly bound rubber fraction reduced it. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: E342–E347, 2012

Key words: rubber; carbon black; filler; composite; swelling

INTRODUCTION

Unsaturated carbon–carbon double bonds (C=C) in a rubber chain of natural rubber (NR), styrene-butadiene rubber, or butadiene rubber (BR) easily reacts with ozone and this reaction leads to the chain scission and the formation of various decomposition products. To protect against ozonation of rubber, waxes and chemical antiozonants such as substituted *para*-phenylenediamines are usually added to rubber compounds.[1,2] Wax compounded into rubber is capable of migrating to the surface of a rubber article, thereby providing protection against ozone attack by forming an impervious barrier on the surface. The ability of a wax to migrate to the surface depends upon the specific wax type, the rubber composition, and the time and temperature. Two types of wax (paraffin and microcrystalline) are used to protect rubber against ozone. Paraffin waxes are mainly constituted by straight chain carbons and are highly crystalline. Waxes, which bloom to the rubber surface and form an inert film to ozone attack, function as physical antiozonants.[3–5] Protection is achieved only when the film is thick enough to provide a barrier against the ozone. Dimauro and coworkers[3] measured the thickness of the paraffin wax film formed on the surface of an NR vulcanizate.

The chemical structures[6,7] and melting points[8] of the normal alkanes (*n*-alkanes) depend on their sizes. The *n*-alkanes with a molecular weight higher than $n\text{-}C_{36}H_{74}$ have a structure of end-chain bending and folding.[7] The melting points of the *n*-alkanes increase with increase in alkyl chain length. The melting points of $n\text{-}C_{21}H_{44}$, $n\text{-}C_{24}H_{50}$, $n\text{-}C_{27}H_{56}$, $n\text{-}C_{30}H_{62}$, $n\text{-}C_{33}H_{68}$, $n\text{-}C_{36}H_{74}$, and $n\text{-}C_{40}H_{82}$ are 39, 51, 58, 63, 70, 75, and 79°C, respectively.[8] The composition of waxes affects the formation of a wax film besides wax content in a rubber article because the alkanes have different structures and melting points depending on their sizes. The amount of *n*-alkanes that migrated to a rubber vulcanizate decreased remarkably until $n\text{-}C_{28}H_{58}$ and then it slightly increased by increasing their molecular weights.[9] Wax film on a rubber article influences migration behaviors of antiozonants.[10–12] Migration rates of antiozonants such as N,N'-disubstituted-*p*-phenylenediamines in rubber vulcanizates containing wax were slower than those in rubber vulcanizates without wax, and the migration rate in a rubber vulcanizate containing wax with a high molecular weight distribution was slower than that in a rubber vulcanizate containing wax with a low one.[10,11] However, the thickness of the wax film hardly affected the migration of antiozonants in rubber vulcanizates.[12]

Correspondence to: S.-S. Choi (sschoi@sejong.ac.kr).

Wax solubility in a rubber article is important to understand wax migration behaviors and wax film formation as well as to determine a proper content of wax in a rubber compound. In this study, we measured wax solubilities of NR composites reinforced with carbon black using wax solution in toluene and investigated a variation of the wax solubility with the carbon black content. Swelling is a good method to add organic materials to a rubber vulcanizate.[13] Carbon black is the most popular reinforcing filler of rubber compounds. The structure and surface chemistry of carbon black are known to affect the physical and chemical properties of rubber compounds.[14,15] The influence of the rubber fractions and bound rubber contents of the carbon black-reinforced NR vulcanizates on the wax solubility was also investigated. Since bound rubber is an important factor in the reinforcement of a rubber compound, the phenomena and effects on the properties of filled rubber compounds and vulcanizates have been extensively studied.[16–22] The properties of bound rubber mainly depend on the characteristics of the filler such as the surface area, structure or morphology, and surface activity. In addition, the filler–polymer interactions also lead to the formation of bound rubber by the physical adsorption, chemisorption, and mechanical interaction. In previous works, we reported the analysis method of wax solubility and influence of wax molecular weights on migration and evaporation of wax.[23,24]

EXPERIMENTAL

Four carbon black-reinforced NR compounds were made of rubber (STR OL, one of standard Thai natural rubbers), carbon black (N330, Columbian Chemicals Korea, Korea), antidegradants (N-phenyl-N′-(1,3-dimethylbutyl)-p-phenylenediamine (HPPD, Kumho Petrochemical, Korea) 1.5 phr and wax (Dongnamyuhwa, Korea) 2.0 phr), cure activators (stearic acid (Dansuk Industrial, Korea) 2.0 phr and ZnO (Hanil Chemical Industrial, Korea) 3.0 phr), and curatives (N-tert-butyl-2-benzothiazole sulfenamide (TBBS, DC Chemical, Korea) 1.8 phr and sulfur (Miwon Chemical, Korea) 1.2 phr). The carbon black contents were 20.0, 40.0, 60.0, and 80.0 phr. The formulations were given in Table I. Mixing of the compound was performed in a Kneader type mixer and the vulcanization was performed at 160°C for 30 min. The sample of 2-mm thickness was cut with the dimension of 1.5 cm × 1.5 cm.

Organic additives remaining in the vulcanized sample (vulcanizate) were removed by extracting with tetrahydrofuran, toluene, and n-hexane for 3, 2 and 1 days, respectively. They were dried for 3 days at room temperature. The weight of the organic materials-extracted sample was measured. Wax

TABLE I
Formulations (phr)

Compound No.	1	2	3	4
STR OL	100.0	100.0	100.0	100.0
N330	20.0	40.0	60.0	80.0
HPPD	1.5	1.5	1.5	1.5
Wax	2.0	2.0	2.0	2.0
ZnO	2.0	2.0	2.0	2.0
Stearic acid	3.0	3.0	3.0	3.0
TBBS	1.8	1.8	1.8	1.8
Sulfur	1.2	1.2	1.2	1.2

solution in toluene was prepared by dissolving 10.5 g wax in 300-mL toluene. The organic materials-extracted sample was soaked in the wax solution for 3 days at 30°C and was dried for 1 day at 70°C to evaporate the solvent. The weight of the wax-dissolved sample was measured. The raw wax solubility (S_{wax}) was calculated by the eq. (1)

$$S_{wax}(\%) = 100 \times (W_{wax} - W_{sample})/W_{sample} \quad (1)$$

where the W_{wax} and W_{sample} are the weights of the wax-dissolved sample and the organic materials-extracted sample, respectively.[23]

Contents of bound rubber in the unvulcanized samples (compounds) were determined by extracting the unbound materials such as ingredients and free rubbers (unbound rubber) with toluene at room temperature or at 90°C for 7 days and with n-hexane at room temperature for 1 day. And then they were dried at room temperature for 2 days. The weights of the samples before and after the extraction were measured and the bound rubber contents were calculated by the eq. (2)

$$R_b(\%) = 100\{W_{fg} - W_t[m_f/(m_f + m_r)]\}/$$
$$\{W_t[m_r/(m_f + m_r)]\} \quad (2)$$

where R_b is the bound rubber content, W_{fg} is the weight of filler and gel, W_t is the weight of the sample, m_f is the fraction of the filler in the compound, and m_r is the fraction of the rubber in the compound.[20–22]

RESULTS AND DISCUSSION

All the experiments were performed three times at least and averaged. The raw wax solubility (S_{wax}) decreased with increase in the carbon black content of the NR composite as shown in Figure 1. The experimental errors were relatively small. Because measurement of the wax solubility was performed using the wax solution in toluene, the S_{wax} must be affected by the solvent swelling ratio. The toluene swelling ratio was measured by soaking the organic
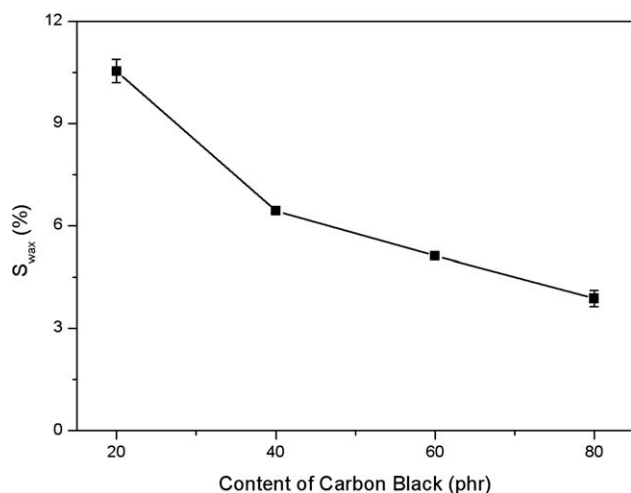
Figure 1 Variation of the raw wax solubility (S_{wax}) of carbon black-filled NR composite with the carbon black content.

materials-extracted sample in toluene. The toluene swelling ratio was obtained by the eq. (3)

$$Q = (W_{toluene} - W_{sample})/W_{sample} \qquad (3)$$

where $W_{toluene}$ and W_{sample} are the weights of the toluene-swollen sample and the organic materials-extracted sample, respectively. The $1/Q$ is usually used as the apparent crosslink density.[25–28] The solvent swelling ratio (Q) decreased with increase in the carbon black content as shown in Figure 2. This means that the crosslink density was increased by increasing the carbon black content. Variations of the S_{wax} and Q with the carbon black content showed similar trends. This implies that the solvent swelling ratio strongly affects the wax solubility behaviors. The S_{wax} and Q values decreased as the carbon black
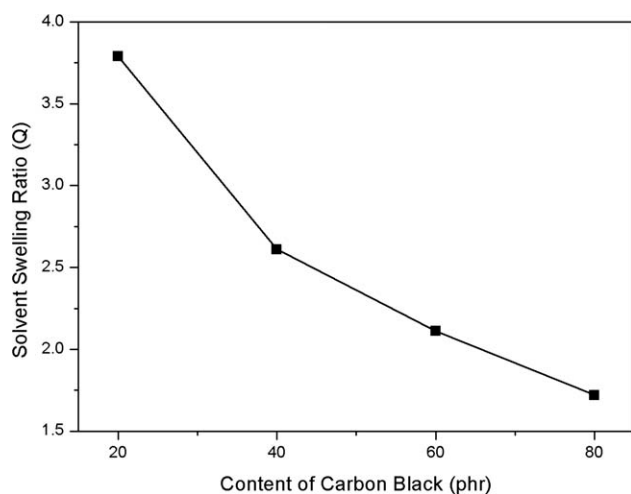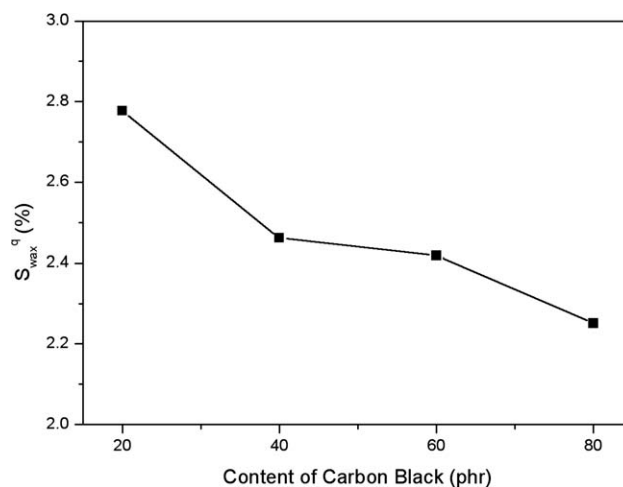
content increased, especially in the range of 20.0 and 40.0 phr. The S_{wax} was corrected with the Q value and the solvent swell-corrected wax solubility (S_{wax}^q) was obtained by the eq. (4)

$$S_{wax}^q = S_{wax}/Q \qquad (4)$$

The S_{wax}^q also decreased with increase in the carbon black content of the rubber specimen as shown in Figure 3. Diffence in the wax solubilities reduced by correction with the solvent swelling ratio.

Rubber chains directly contact with carbon black during mixing and bound rubbers are formed. Most of carbon black particles in the rubber composite will be shielded by bound rubber chains, so the solvent and wax molecules cannot directly contact to the carbon black particles. In general, some rubber chains are bound to filler particles and they are not extracted with a good solvent, which is called bound rubber. The wax solubility was corrected with the rubber fraction and bound rubber content to investigate the influencing parameters on the wax solubility. Bound rubber is composed of loosely and tightly bound ones.[20–22,29–32] 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.[21,29] The tightly bound rubber is much less mobile than the loosely one.[21,29] In general, measurement of the bound rubber content is performed under the restricted condition at room temperature and under the static condition to prevent the bound rubber (especially the loosely bound rubber) from extracting.[20–22] 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. Bound

Figure 2 Variation of the solvent swelling ratio (Q) of carbon black-filled NR composite with the carbon black content.

Figure 3 Variation of the solvent swell-corrected wax solubility (S_{wax}^q) of carbon black-filled NR composite with the carbon black content.
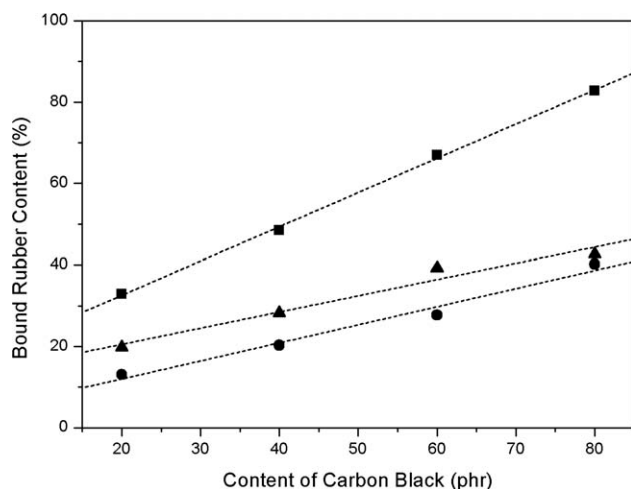
Figure 4 Variation of the total and tightly bound rubber contents of carbon black-filled NR compounds with the carbon black content. Squares, circles, and triangles indicate the total, tightly, and loosely bound rubber contents, respectively.

rubber contents measured at room temperature and 90°C were total and tightly bound rubber contents, respectively.[21,33] Loosely bound rubber content was the difference between the total and tightly bound rubber contents.[21,33]

Total, tightly, and loosely bound rubber contents linearly increased with the carbon black content and were compared as shown in Figure 4. The linear curve fitting equations were $y = 0.841x + 15.8$ ($r = 0.999$), $y = 0.444x + 3.15$ ($r = 0.990$), and $y = 0.397x + 12.6$ ($r = 0.982$) for the total, tightly, and loosely bound rubber contents, respectively. This means that the total, tightly, and loosely bound rubber contents increased 8.41, 4.44, and 3.97% every 10.0 phr carbon black, respectively. Most wax may be dissolved in only rubber not carbon black, and wax solubility behaviors in the tightly and loosely bound rubber regions may be different from the free rubber (unbound rubber) region. Thus, the wax solubilities were corrected with the rubber fraction, total bound rubber content, and tightly bound rubber content as shown in Figure 5.

The rubber fraction-corrected wax solubility ($S_{wax}^r(rf)$) was obtained by the eq. (5)

$$S_{wax}^r(rf) = S_{wax}/X(rf) \qquad (5)$$

where $X(rf)$ is the rubber fraction of the carbon black-filled NR composite. Rubber fractions of the carbon black-filled samples were 100/120, 100/140, 100/160, and 100/180 for the carbon black contents of 20.0, 40.0, 60.0, and 80.0 phr, respectively. The $S_{wax}^r(rf)$ was based on an assumption that wax solution penetrated through all rubber regions including the bound rubber regions. The total bound

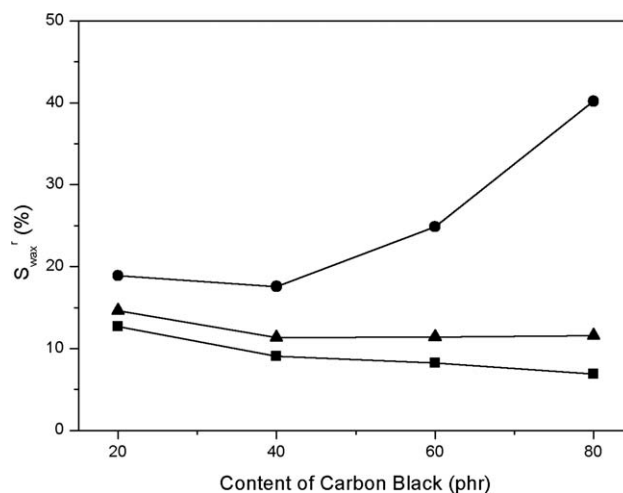rubber content-corrected wax solubility ($S_{wax}^r(br)$) was obtained by the equation (6)

$$S_{wax}^r(br) = S_{wax}/[X(rf) \times (1 - R_b(total)/100)] \qquad (6)$$

where $R_b(total)$ is the total bound rubber content. The $S_{wax}^r(br)$ was based on an assumption that wax solution penetrated only into the unbound rubber regions. The tightly bound rubber content-corrected wax solubility ($S_{wax}^r(tb)$) was obtained by the eq. (7)

$$S_{wax}^r(tb) = S_{wax}/[X(rf) \times (1 - R_b(tight)/100)] \qquad (7)$$

where $R_b(tight)$ is the tightly bound rubber content. The $S_{wax}^r(tb)$ was based on an assumption that wax solution penetrated into the loosely bound rubber region as well as the unbound rubber region.

The $S_{wax}^r(rf)$ continuously decreased with increase in the carbon black content as shown in Figure 5. Difference in the $S_{wax}^r(rf)$s of the samples with different carbon black contents reduced related to the the S_{wax}s. Difference in the S_{wax}s of the samples with the carbon black contents of 20 and 80 phr was 2.7 times, whereas difference in the $S_{wax}^r(rf)$s was 1.8 times. Variation of the $S_{wax}^r(br)$ showed a big difference from the $S_{wax}^r(rf)$ variation. The $S_{wax}^r(br)$ decreased from 20 phr to 40 phr of the carbon black content, but it notably increased after 40 phr. This indicates that wax could be dissolved into some bound rubber regions. Since tightly bound rubbers were not extracted by a good solvent even at high temperature of 90°C for several days, it is reasonable that solvent and wax do not deeply penetrate into the tightly bound rubber region. Thus, we can say

Figure 5 Variation of rubber-corrected wax solubility (S_{wax}^r) of carbon black-filled NR composite with the carbon black content. Squares, circles, and triangles indicate the corrections with rubber fraction ($S_{wax}^r(rf)$), total bound rubber content ($S_{wax}^r(br)$), and tightly bound rubber content ($S_{wax}^r(tb)$), respectively.
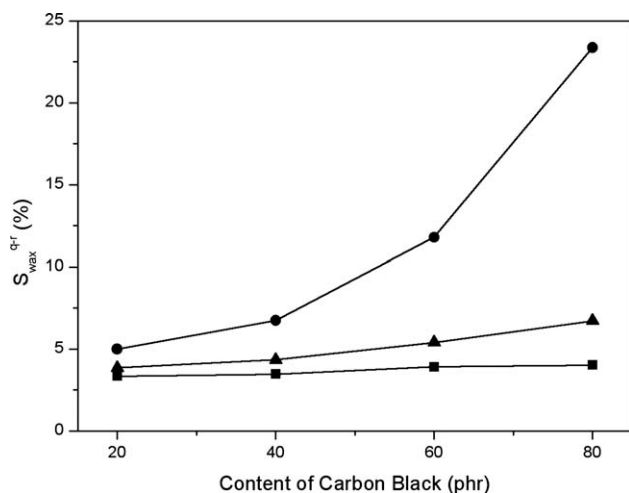
Figure 6 Variation of solvent swell and rubber-corrected wax solubility (S_{wax}^{q-r}) of carbon black-filled NR composite with the carbon black content. Squares, circles, and triangles indicate the corrections with solvent swelling ratio-rubber fraction (S_{wax}^{q-r}(rf)), solvent swelling ratio-total bound rubber content (S_{wax}^{q-r}(br)), and solvent swelling ratio-tightly bound rubber content (S_{wax}^{q-r}(tb)), respectively.

that wax is dissolved into loosely bound rubber regions. The S_{wax}^r (tb) slightly decreased from 20 to 40 phr of the carbon black content and then stayed a constant value. Constant value of the S_{wax}^r (tb) from 40 to 80 phr of the carbon black content may be a concrete evidence that wax is dissolved into the loosely bound rubber region as well as the unbound rubber region. Difference in the maximum and minimum S_{wax}^r (tb)s was 1.3 times.

As we can see, solvent swell and free rubber fraction influenced on the wax solubility. We corrected the wax solubility by both of the solvent swelling ratio and free rubber fraction. All the corrected wax solubilities by both of the solvent swelling ratio and free rubber fraction increased with increase in the carbon black content as shown in Figure 6.

$$S_{wax}^{q-r}(rf) = S_{wax}/[Q \times X(rf)] \quad (8)$$

$$S_{wax}^{q-r}(br) = S_{wax}/[Q \times X(rf) \times (1 - R_b(total)/100)] \quad (9)$$

$$S_{wax}^{q-r}(tb) = S_{wax}/[Q \times X(rf) \times (1 - R_b(tight)/100)] \quad (10)$$

The solvent swelling ratio and rubber fraction-corrected wax solubility (S_{wax}^{q-r} (rf)) slightly increased with increase in the carbon black content. The solvent swelling ratio and tightly bound rubber content-corrected wax solubility (S_{wax}^{q-r} (tb)) increased more than the S_{wax}^{q-r} (rf). The solvent swelling ratio and total bound rubber content-corrected wax solubility (S_{wax}^{q-r} (br)) steeply increased with increase in the carbon black content. The S_{wax}^{q-r} (br) increases with the

increase of R_b(total). Level of the increment of the R_b(total) with the carbon black content is larger than that of the R_b(tight) by about twice (Fig. 4). Hence, the S_{wax}^{q-r} (br) notably increases with the increase of the carbon black content compared with the S_{wax}^{q-r} (rf) and S_{wax}^{q-r} (tb). The increasing wax solubility with the carbon black content is not acceptable because wax is dissolved into rubber not filler. The experimental results can lead to a conclusion that the solvent swell affects the wax solubility but relation between the solvent swelling ratio and the wax solubility is not linear.

CONCLUSIONS

The raw wax solubility (S_{wax}) decreased with increase in the carbon black content of the NR composite. Variations of the S_{wax} and solvent swelling ratio (Q) with the carbon black content showed similar trends. The solvent swell-corrected wax solubility (S_{wax}^q) also decreased with increase in the carbon black content. It was found that wax was dissolved well into the loosely bound rubber region. Positive factors to enhance the wax solubility were the solvent swelling ratio and the unbound and loosely bound rubber contents, while the negative parameter was the tightly bound rubber content.

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