



Influence of Wax Molecular Weights on Wax Migration and Evaporation of Rubber Vulcanizates at Room Temperature

Song-Hee Im and Sung-Seen Choi[†]

Department of Chemistry, Sejong University, 98 Gunja-dong, Gwangjin-gu, Seoul 143-747, Korea
(Received June 12, 2009, Revised June 23, 2009, Revised & Accepted August 24, 2009)

상온 노화 후 고무가황물에서 왁스의 이동과 증발에 미치는 왁스의 분자량 분포

임 송 희 · 최 성 신[†]

세종대학교 화학과

(2009년 6월 12일 접수, 2009년 6월 23일 1차 수정, 2009년 8월 24일 수정 및 채택)

ABSTRACT : Ozone caused the crack on the surface of a rubber article by oxidation of double bond at room temperature. Wax migrates to the surface of a rubber article and makes a physical barrier to prevent process of ozonation. We investigated change of molecular weight distribution of waxes in unfilled NR, SBR, and BR vulcanizates before and after aging at room temperature for 6 months. Migration and evaporation behaviors of wax in a rubber article at ambient conditions help understand a role of wax as an antidegradant and appearance contamination of a rubber article. The relative intensity distribution of *n*-alkanes of the NR specimen after the aging was shifted to higher molecular weight compared with the relative intensity distribution before the aging, while those of the SBR specimen before and after the aging did not show a big difference.

요약 : 오존은 상온에서 폴리머 이중 결합의 산화작용을 활발하게 하여 표면 갈라짐을 유발시킨다. 왁스는 고무 표면으로 이동하여 물리적 방어막을 형성하여 오존의 작용을 방지한다. 비보강 NR, SBR, BR 가황물을 상온에서 6개월간 노화 시켜 노화 전후의 왁스의 분자량 분포 변화를 조사하였다. 상온 조건에서 고무 가황물에 있는 왁스의 이동과 증발 거동은 노화방지제로서의 왁스의 역할과 고무 제품의 외관 오염을 이해하는데 도움을 준다. NR 시험편에서 알칸의 상대 세기 분포는 노화 후 고분자량쪽으로 이동하였으나 SBR 시험편의 경우에는 노화 전후의 분자량 분포 모양에는 큰 차이가 없었다.

Keywords : wax, molecular weight, rubber vulcanizate, evaporation, migration

I. Introduction

Ozone attack on a rubber article causes characteristic cracking perpendicular to the direction of applied stress. This degradation is caused by reaction of ozone with the carbon-carbon double bonds (C=C) in the rubber chains. These reactions lead to chain scission and the formation of various decomposition products. Wax or chemical antiozonants are added to unsaturated rubbers to control the effects of rubber ozonation.¹

Two types of wax used to protect rubber against ozone; paraffinic and microcrystalline. Paraffinic wax which was used in this study is mainly constituted by straight chain hydrocarbons of relatively low molecular weight of about 350-420. Because of their linear structures they are highly crystalline and form large crystals melting in the range of 38-74 °C.

Waxes which bloom to the rubber surface and form a film inert to ozone attack function as physical antiozonants.² Protection is achieved only when the film is thick enough to provide a barrier to the ozone. Thicker films can ensure better protection but the appearance of a rubber article is contaminated. Thickness of the bloomed film of wax depends on both solubility and diffusion rate of the wax in rubber. These parameters are both temperature and time dependent.³

Blooms occur whenever the solubility of a wax in a rubber article is reduced. At temperatures lower than 40 °C only small molecules can migrate and by reducing the temperature the reduced solubility of the waxes causes an increase of their bloom. Additionally the small sizes of the low molecular weight molecules permit them to migrate rapidly to the surface, in spite of the lower temperature.³ As time goes by, waxes which migrate to the surface vaporize. Experiments of the evaporation of the normal alkanes dependent on molecular

[†]Corresponding Author. E-mail: sschoi@sejong.ac.kr

weights were carried out by aging at room temperature for 6 months. We compared molecular weight distributions of wax remained in a rubber vulcanizate before and after aging at ambient temperature for six months.

II. Experimental

In order to investigate the migration behaviors of wax to the surface in a rubber vulcanizate, three unfilled rubber compounds of natural rubber (NR), styrene-butadiene rubber (SBR), and butadiene rubber (BR) were prepared. SMR20, SBR1500 (Kumho Petrochemical Co. of Korea), BR01 (Kumho Petrochemical Co. of Korea) were used as NR, SBR, and BR, respectively. Same cure system (ZnO 2.0 phr, stearic acid 2.0 phr, N-t-butylbenzothiazole sulfonamide (TBBS) 1.6 phr, and sulfur 1.4 phr) was employed. The rubber vulcanizates were prepared by curing at 160 °C in a press mold.

The sample of 2 mm thickness was cut with the dimension of 1.5×1.5 cm². Wax was added by swelling method using wax solution in toluene. Wax solution in toluene was prepared by dissolving 10.5 g wax in 300 mL toluene. Organic additives remaining in the sample were removed by extracting with THF, 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. The organic 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 wax-dissolved sample was aged at room temperature for 6 months.

The waxes remained in the rubber vulcanizates before and after aging were extracted with toluene for 5 hr in 70 °C oven. The extracted wax was analyzed using GC-FID and the molecular weight distributions of wax remained in the sample before and after aging were compared. GC analyses were carried out on a Acme 6000M GC (Young Lin Instrument Co., Korea). HP-5 capillary column (30 m length, 0.25 mm inner diameter, 0.25 μm film thickness) was used. Injector and detector temperatures of GC were all 250 °C. The GC oven temperature program was as follows: (1) The initial temperature was 70 °C and kept for 3 min. (2) The temperature was then increased from 70 to 300 °C at a rate of 10 °C/min. (3) Final temperature was maintained for 10 min.

III. Results and Discussion

Wax is a mixture of normal alkanes and their isomers. Since wax used in this study is mainly composed of normal alkanes, only the *n*-alkanes of wax were employed as the experimental targets. The molecular weight distribution of the raw wax was shown in Figure 1. The wax had a molecular weight distribution from C₁₉H₄₀ to C₄₂H₈₆ and the maximum peak was

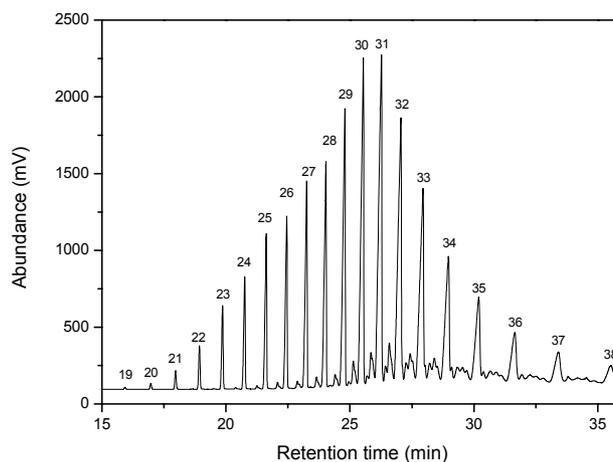


Figure 1. GC chromatogram of the raw wax used in this study. The numbers written above the peaks indicate the number of carbon atoms of the *n*-alkanes.

C₃₁H₆₄. Because amounts of C₁₉H₄₀, C₂₀H₄₂ and C₃₆H₇₄ to C₄₂H₈₆ were very small, we discussed about the waxes of C₂₁H₄₄ - C₃₅H₇₂. In general, molecular weight distribution of wax in a rubber vulcanizate is different from the raw wax used for manufacturing the rubber vulcanizate because some waxes are evaporated and the evaporation behaviors depend on the molecular weights of waxes. We dissolved wax into the rubber samples by swelling method as described in the experimental section to prevent experimental errors by different initial wax distributions. Weights of wax dissolved in the NR, SBR, and BR vulcanizates were about 10 wt%.

Waxes were extracted from the samples before and after the aging at room temperature for 6 months and relative intensity distributions of *n*-alkanes were analyzed with GC-FID. The relative intensity distributions of *n*-alkanes before and after the aging were compared as shown in Figures 2, 3, and 4 for the NR, SBR, and BR vulcanizates, respectively. The relative intensity distributions of *n*-alkanes before and after the aging of the NR vulcanizate showed a big difference, while those of the SBR vulcanizate were the similar shape. For the NR vulcanizate, the relative intensity distribution of *n*-alkanes after the aging was shifted to the higher molecular weight compared with the relative intensity distribution before the aging. This is because of difference in the wax migration and evaporation behaviors depending on their sizes. For the BR vulcanizate, similarly to the NR vulcanizate, the relative intensity distribution of *n*-alkanes after the aging was on the whole shifted to the higher molecular weight compared with the relative intensity distribution before the aging, but degree of the shift was very small compared with the NR vulcanizate.

Wax migrates to the surface of a rubber article and evaporates. Evaporation of *n*-alkanes depends on their sizes. The

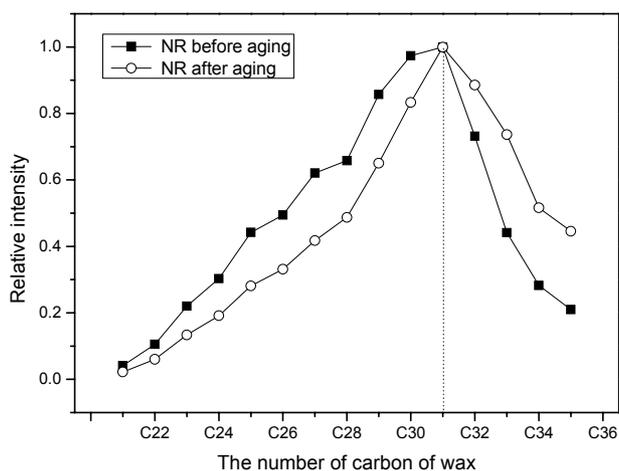


Figure 2. Relative intensity distributions of *n*-alkanes of the NR vulcanizate before (■) and after (○) aging at room temperature for 6 months.

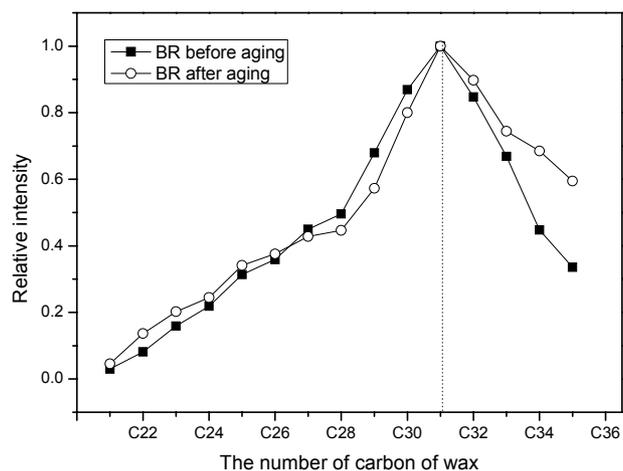


Figure 4. Relative intensity distributions of *n*-alkanes of the BR vulcanizate before (■) and after (○) aging at room temperature for 6 months.

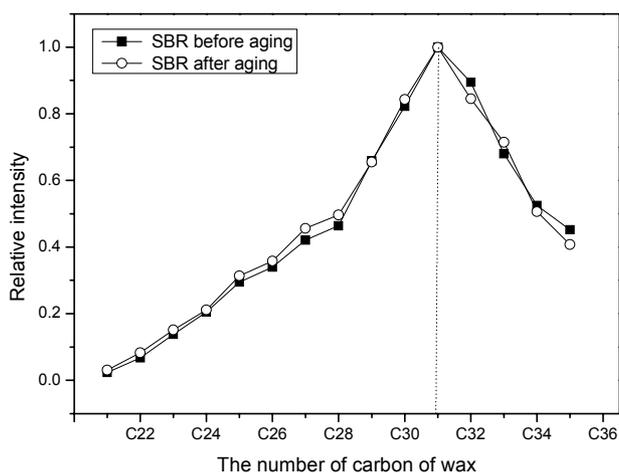


Figure 3. Relative intensity distributions of *n*-alkanes of the SBR vulcanizate before (■) and after (○) aging at room temperature for 6 months.

amount of the *n*-alkanes that evaporated at room temperature was continuously decreased by increasing their molecular weight. The decrement of the amount of evaporated *n*-alkanes with an increase of their molecular weights can be explained by their melting and boiling points and fusion and evaporation enthalpies. Won⁴ proposed the fusion temperatures of normal paraffins (equation (1)) and relation between the fusion temperature and the fusion enthalpy (equation (2)).

$$T_i^f = 374.5 + 0.02617MW_i - 20172/MW_i \quad (MW_i \leq 450 \text{ g/mol})$$

$$T_i^f = 411.4 - 32326/MW_i \quad (MW_i \leq 450 \text{ g/mol}) \quad (1)$$

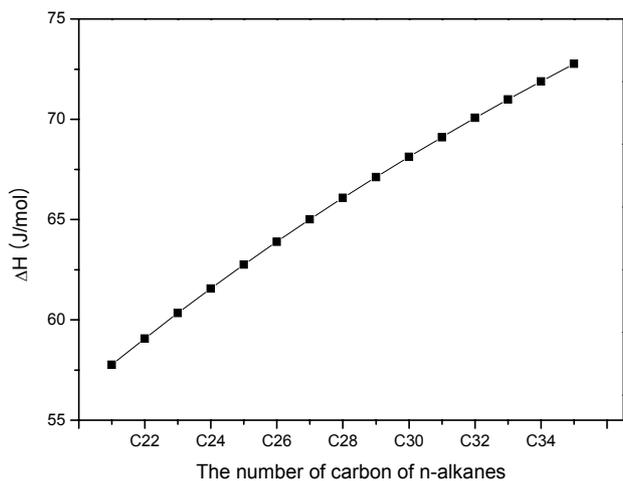


Figure 5. Variation of enthalpy of evaporation of *n*-alkane as a function of the carbon atom number.

where MW_i is the molecular weight of *i*-paraffin and T_i^f is the fusion temperatures of *i*-paraffin.

$$\Delta H_i^f = 0.4998MW_i \cdot T_i^f \quad (\text{for } C_{21}H_{44} - C_{38}H_{78}) \quad (2)$$

where ΔH_i^f is the fusion enthalpy of *i*-paraffin. As shown in the equations (1) and (2), the melting temperature and fusion enthalpy continuously increase with increase in the molecular weight of wax.

Melting and boiling points and fusion and evaporation enthalpies of *n*-alkane increase with increase in the molecular weight as shown in equations (1) and (2). Figure 5 shows variation of the enthalpy of vaporization⁵ with the wax size.

The *n*-alkane with a low melting point may evaporate better than that with a high one. Amounts of evaporated waxes of *n*-C₂₂H₄₆ to *n*-C₂₈H₅₈ from wax film of 8 μm thickness after thermal aging at 60 and 80 °C for 6 days were 2 - 80%.⁶ The evaporation increased notably by decreasing the molecular weight of wax. For the NR specimen, evaporation rate of wax decreased with increase in the molecular weight of wax as shown in Figure 2. This can be explained by the enthalpy of vaporization of wax as shown in Figure 5. The enthalpy of vaporization increases as the molecular weight of wax increases. Thus, when wax on the surface of the NR specimen evaporates under same environmental conditions, wax with a low molecular weight will evaporate better than wax with a high one. This phenomenon is also observed at the SBR and BR specimens as shown in Figures 2 and 3, respectively. But evaporation difference according to the molecular weights was lower relative with the NR specimen. The migration of the normal alkanes in the NR vulcanizate is more sensitive to the change of the molecular size of the normal alkanes than those in the BR and SBR vulcanizates.⁶ The migration behaviors of wax in a rubber article is strictly affected by the evaporation of wax from the surface.⁶ The intermolecular interactions between migrants and matrices of rubber and filler are principal factors influencing on the migration of antiozonants in a rubber vulcanizate.⁷⁻⁹ The migration rates of migrants become slower and slower as the intermolecular interactions become stronger and stronger.

Difference in the molecular weight distributions of wax in the NR specimen before and after the aging at room temperature for 6 months was very different from the SBR specimen. Variations of the relative amounts of evaporated waxes with the molecular weight were plotted as shown in Figure 6 to

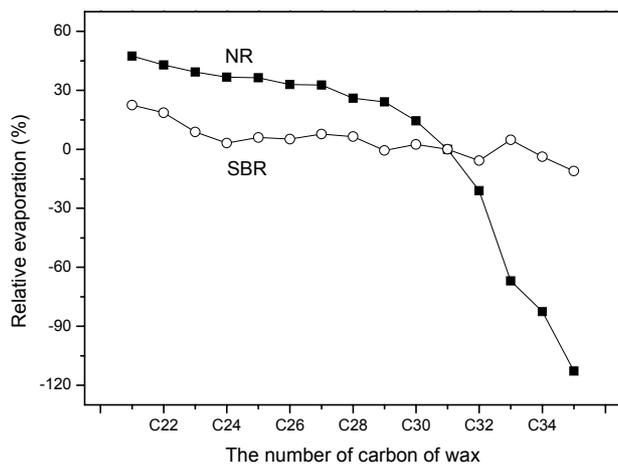


Figure 6. Variations of amounts of evaporated *n*-alkanes of the NR (■) and SBR (○) vulcanizates after aging at room temperature for 6 months with the molecular weight of wax. The C₃₁H₆₄ is the reference.

compare consumption behaviors of waxes of the NR and SBR specimens in detail. The most abundant wax of C₃₁H₆₄ was employed as a reference because it is very hard to purchase or obtain each ultra-pure *n*-alkane to make calibration curve for quantitation analysis. We compared the consumed amounts of the waxes after the aging at room temperature for 6 months by employing C₃₁H₆₄ as a reference. We assumed that the consumed amount of C₃₁H₆₄ was zero. For the NR specimen, the evaporation rate slightly decreased until C₂₈H₅₈ or C₂₉H₆₀ and then steeply decreased with increase in the molecular weight of wax. This implies that waxes with low molecular weights are fast evaporated and only waxes with high molecular weights are remained in the rubber sample when an NR article was used for a long time. For the SBR specimen, the evaporation rate slightly decreased with increase in the molecular weight of wax and the difference was small. This implies that molecular weight distribution of waxes is not largely changed compared with the initial molecular weight distribution although a SBR article is used for a long time. Migration and evaporation behaviors of wax in a rubber article at ambient conditions help understand a role of wax as an antidegradant and appearance contamination of a rubber article.

References

1. S.-S. Choi, "Wax barrier effect on migration behaviors of antiozonants in NR vulcanizate", *Elastomer*, **34**, 147 (1999).
2. P. B. Sulekha, R. Joseph, and S. Prathapan, "Synthesis and characterization of chlorinated paraffin wax-bound paraphenylenediamine antiozonant and its application in natural rubber", *J. Appl. Polym. Sci.*, **81**, 2183 (2001).
3. F. Cataldo, "On the ozone protection of polymers having non-conjugated unsaturation", *Polym. Degrad. Stab.*, **72**, 287 (2001).
4. K. W. Won, "Thermodynamics for solid-liquid-vapor equilibria: wax phase formation from heavy hydrocarbon mixtures", *Fluid Phase Equilib.*, **30**, 265 (1986).
5. <http://www.chemspider.com/Chemical-Structure.11897.html>, 11899.html, 12017.html, 12072.html, 11900.html, 11901.html, 11146.html, 11902.html, 11903.html, 12018.html, 11904.html, 10542.html, 11905.html, and 24702.html and <http://www.chemspider.com/Search.aspx?q=C35H72>.
6. S.-S. Choi, "Migration behaviors of wax to surface in rubber vulcanizates", *J. Appl. Polym. Sci.*, **73**, 2587 (1999).
7. S.-S. Choi, "Migration of antidegradants to the surface in NR and SBR vulcanizates", *J. Appl. Polym. Sci.*, **65**, 117 (1997).
8. S.-S. Choi, "Influence of silica content on migration of antidegradants to the surface in NR vulcanizates", *J. Appl. Polym. Sci.*, **68**, 1821 (1998).
9. S.-S. Choi, "Migration of antidegradants to the surface in NR vulcanizates: Influence of content of carbon black", *Bull. Kor. Chem. Soc.*, **19**, 170 (1998).