



A New Method to Identify PCA Oil Type through Solvent Extraction and Separation Skills in a SBR Vulcanizate

Min-Saeng Kim, Kyung-Suk Sohn, Jung-Hun Lee, Ik-Sik Kim[†], and Sung-Seen Choi*

Aero Technology Research Institute, P.O. Box 304-160, Geomsa-dong, Dong-gu, Daegu, Korea

*Department of Chemistry, Sejong University, 98 Gunja-dong, Gwangjin-gu, Seoul 143-747, Korea

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SBR 가황물에서 용매추출 및 분리에 의한 PCA 오일 Type 확인법

김민생 · 손경숙 · 이중훈 · 김익식[†] · 최성신*

공군 항공기술연구소, *세종대학교 화학과

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ABSTRACT : More than 3 wt% of polycyclic aromatics (PCAs) in process oil is known to cause skin cancer. The criterion of distinguishing between low PCA oil and high PCA oil is based on 3 wt% of PCA. High PCA oil is called as a carcinogen like distillate aromatic extract (DAE). Low PCA oil is considered as safety oils like treated distillate aromatic extract (TDAE), mild extract solvate (MES), and paraffinic oil. Four types of process oils such as DAE, TDAE, MES, and paraffinic oil purified by solvent extraction and separation skills from SBR vulcanizates were measured by FT-IR techniques. The effects of rubber chemicals such as N-1,3-dimethylbutyl-N'-phenyl-p-phenylnenediamine (HPPD), polymerized 2,2,4-trimethyl-1,2-dihydroquinoline (TMDQ), paraffin wax as antidegradants, and processing aid like Structol 40MS on paraffinic oil from SBR vulcanizates were also studied. The type of low or high PCA was identified by the relative abundance of absorbance at the aromatic substitution patterns of 864, 810, and 754 cm^{-1} and at the paraffinic or naphthenic pattern of 721 cm^{-1} .

요약 : 공정오일 내 다핵성 방향족 화합물(PCA)은 무게함량 대비 3%이상 함유한 경우 피부암을 일으키는 것으로 알려졌다. 저함량과 고함량 PCA 오일의 구분 기준은 PCA 함량 3%에 근거한다. 기준 함량 이상이면 발암성 물질인 고함량 PCA 오일로 DAE가 있으며, 기준 함량 이하이면 인체에 안전한 저함량 PCA 오일로 TDAE, MES, 파라핀 오일이 이에 속한다. 상기 4종류의 공정오일을 적용한 SBR 가황물에 용매 추출 및 분리로 오일을 정제한 후, FT-IR 분광 기술을 이용하여 PCA 오일 종류를 결정하였다. 그리고 파라핀 오일이 적용된 SBR 가황물에서 고무 약품인 HPPD, TMDQ, 왁스, 공정조제(Structol-40MS)의 오일에 대한 영향을 연구하였다. 분리 정제된 오일로부터 저함량과 고함량 PCA 오일 구분은 방향족 치환체 흡수영역인 파수 864, 810, 754 및 파라핀 또는 나프텐 흡수영역인 파수 721의 상대적인 흡수세기로 확인할 수 있었다.

Keywords : FT-IR, polycyclic aromatics, PCA, oil, oil type, separation, extraction

I. Introduction

The tire and rubber industry has predominantly used distillate aromatic extracts (DAE) for the oil extender of synthetic rubbers and plasticiser of rubber compounds in tire manufacturing process because the high aromaticity of DAE gives excellent rubber solubility. However, several studies in Sweden reporting a potential carcinogenicity of these oils after tumors have observed in various mice skin painting tests.^{1,2,3} The EU Dangerous Substance Directive classifies DAE as carcinogenic due to the high levels of polycyclic aromatics (PCAs) present, and requires them to be labeled with "a skull and crossbones"

and the phase R45 "May cause cancer".⁴ The Directive states that any DAE or related material with a PCA content of greater than 3 wt%, as determined by the IP 346 DMSO (dimethyl sulphoxide) method, must have this warning label. The oils including more than 3 wt% PCA are called as high PCA, like DAE and are known to be a potential carcinogen. The oils below it are called as low PCA, like treated distillate aromatic extract (TDAE), mild extracted solvate (MES), or paraffinic oil and are considered as safety oils. The global market place is increasingly demanding safe process oils to reduce the environmental impact of tires. The EU Carcinogens Directive 90/394/EEC comments on the reduction and replacement of carcinogen materials.⁵ In addition, the health and environmental concerns over the use of DAE in tire compounds were high-

[†] Corresponding Author. E-mail: iskim2@airforce.mil.kr

lighted in the Swedish National Chemicals Inspectorate report, published in 1994.⁶

So far, three analytical techniques using IP 346, HPLC, and GC/MS to detect PCA in raw oil have been known.⁷ These methods provide very divergent results since they measure completely different things. Therefore, it is hard and unreasonable to compare such results. IP 346 is used to determine which oils were labeled according to EU regulation.⁸ The limit where labeling becomes obligatory is 3 wt%. What IP 346 measures is the content of substances soluble in DMSO. This method is used to know if oil is a carcinogen because this method shows good correlation with the incidence of skin cancer in mice. High performance liquid chromatograph (HPLC) method is quicker than IP 346 following several cumbersome extraction steps and emitting a fairly unpleasant odor. This method measures the amount of more polar aromatics than markers such as naphthalene or anthracene. Gas chromatograph (GC) measures the content of individual polyaromatic hydrocarbons (PAHs) and the PAH profile of the oil. However, GC does not give us the absolute value, either. All components in oil cannot be effectively separated by GC column because it includes a lot of mixtures. If we want to know which oils may cause cancer, then we get the answer through IP 346. An exact technique to measure the total PCA content in process oil has not been known yet. With HPLC or GC method that includes all polycyclic aromatics, a good result can be obtained to some degree. Recently, Swedish Government requires the snow tire using low PCA oil in tire tread. Most of tire companies develop and supply tire satisfying this requirement. At this time, it is important to find out a method to identify the type of PCA oil in tire. However, a component of tire contains many kinds of organic additives, such as process oils, activators, curing agents, processing aids, and antidegradants. Of component ingredients, processing aids and antidegradants including aromatic or paraffinic materials must be completely eliminated to identify low or high PCA oil. Therefore, it is important to select a proper solvent to extract only process oil throughly.

In the present work, we show the purification of process oil from various rubber chemicals through 3-step solvent extraction from SBR vulcanizates and can rapidly and easily determine the type of PCA by FT-IR techniques. We also study the effects of antidegradants such as 6PPD and TMDQ, paraffin wax, and processing aid such as Structol 40MS on paraffinic oil from SBR vulcanizates in determining the process oil type.

II. Experimental

Four types of the process oils such as Tyrex 20, Prorex 15, aromatic, and paraffinic are used as standard materials. Tyrex 20 and Prorex 15 are purchased from ExxonMobil Co. in France. Aromatic and paraffinic oil are purchased from Michang Petroleum Co. in South Korea. The typical characteristics for standard oils are listed as described in Table 1. Carbon type compositions (C_A , C_N , and C_P) were measured according to ASTM D 2140. PCA content was determined by IP 346 method. Aromatic oil is a DAE type as a carcinogen containing high concentration (14.4wt%) of polycyclic aromatics. Tyrex 20 is a TDAE product treated with hydrogenation or further severe solvent extraction of DAE as a non-carcinogen. Prorex 15 is a MES product as a non-carcinogen. Paraffinic oil obtained by a vacuum distillation contains the least polycyclic aromatic component (0.4wt%) as a non-carcinogen. Four standard samples are measured by FT-IR spectroscopy at $1000\sim 650\text{ cm}^{-1}$ to identify oil type. The relative absorption abundance of standard oils at 864, 810, 754, and 721 cm^{-1} was used to identify oil type.

Eight carbon black-filled styrene-butadiene rubber (SBR 1502) compounds were prepared. The formulations are given in Table 2. Five compounds (S1, S2, S3, S4, and S5) were made of SBR 1502, carbon black (N330), cure activators, curatives, paraffin wax, and paraffinic oil with/without antidegradants such as TMDQ and/or HPPD, or processing aid such as Structol 40MS. The first five vulcanizates (S1, S2, S3, S4, and S5) were made to investigate the effect of anti-

Table 1. Typical Characteristics for Standard Oils

Process Oil	Aromatic	Paraffinic	Tyrex 20	Prorex 15
Types	DAE	-	TDAE	MES
Relative Density at 15 °C	0.993	0.885	0.965	0.850
Kinetic Viscosity at 100 °C (cSt)	18	8	20	15
PCA Content (wt%)	14.4 (high)	0.4 (low)	1.8 (low)	1.6 (low)
Aromatic Component, C_A (wt%)	40	6	27	15
Naphthenic Component, C_N (wt%)	33	32	26	29
Paraffinic Component, C_P (wt%)	27	62	47	56

Table 2. Compound Formulations

Compound No.	S1	S2	S3	S4	S5	S6	S7	S8
SBR 1502	100	100	100	100	100	100	100	100
N330	50	50	50	50	50	50	50	50
ZnO	5	5	5	5	5	5	5	5
TMDQ	0	2	0	2	0	0	0	0
HPPD	0	0	2	2	0	0	0	0
Wax	2	2	2	2	2	2	2	2
Structol 40MS	0	0	0	0	2	0	0	0
Stearic Acid	2	2	2	2	2	2	2	2
Paraffinic	40	40	40	40	40	0	0	0
Aromatic	0	0	0	0	0	40	0	0
Tyrex 20	0	0	0	0	0	0	40	0
Prorex 15	0	0	0	0	0	0	0	40
Sulfur	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
TBBS	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2

SBR 1502: styrene-butadiene rubber

N330: carbon black

Structol 40MS: trade name of Bayer, a homogenizing agent

TMDQ: polymerized 2,2,4-trimethyl-1,2-dihydroquinoline, antioxidant

HPPD: N-1,3-dimethylbutyl-N'-phenyl-*p*-phenylenediamine, antiozonant

TBBS: N-*tert*-butyl-2-benzothiazole sulfenamide, cure accelerator

degradants and processing aid. Four compounds (S4, S6, S7, and S8) consist of SBR 1502, carbon black, cure activators, curatives, and with different types of process oils such as paraffinic, DAE, TDAE, and MES, respectively. Four vulcanizates are used to confirm the possibility of determining oil type.

Mixing of the compounds was performed in a banbury mixer at the same rotor speed of 40 rpm for master batch (MB) and final mixing (FM) stages, respectively. The initial temperatures of the mixer were 110 °C and 80 °C for the MB and FM stages, respectively. The MB compound included rubber, carbon black, process oil, cure activators (stearic acid and ZnO) and antidegradants (HPPD, paraffin wax, or TMDQ). The MB compound was discharged at 145 °C. The FM compounds were prepared by mixing the MB compounds with the curatives (TBBS and sulfur) and were dumped at 110 °C. Eight vulcanizates were prepared by curing at 160 °C for 20 min.

For purification of process oil from SBR vulcanizates, each sample was cut into 1 mm³ in size and about 0.1 g of sample was weighted and extracted with 1.5 mL of acetonitrile (ACN) in a vial at 80 °C oven for 4 h. This process was to eliminate the interference of antidegradants in analyzing oil type by FT-IR spectroscopy. The residual rubber was washed twice with ACN and dried at 80 °C oven for 20 min. And then, the residue was dissolved in *n*-hexane to extract simultaneously

process oil and paraffin wax. The hexane extract is evaporated, dissolved in acetone, and then cooled to -15 °C for eliminating wax. The acetone solution is evaporated to be concentrated at 80 °C oven for 10 min. The oil types of concentrated samples were measured and identified by FT-IR spectroscopy. Extracts in all steps are also identified with GC.

FT-IR spectra were taken on film, using a Bruker FT-IR spectroscopy (IFS 85). The samples were scanned from 400~4000 cm⁻¹ with a resolution 4 cm⁻¹ and the average of ten scans for each sample was taken for the measurement. The chromatograms were obtained by using GC (HP 5890 Series II) equipped with automatic liquid sampler (HP 6890 Series) and integrator (HP 3396 Series III). The conditions for measurement are as follows; injector temperature (250 °C), injection volume (1 μL), split ratio (300:1), column (20 m x 0.2 mm i.d., Ultra-1), oven temperature (150~300 °C, 10 °C/min), and flame ionization detector (FID) temperature (260 °C).

III. Results and Discussion

1. Standard Oils

Process oil helps to mix polymer well with filler in a banbury mixer. Process oils are incorporated into rubber during mixing to ease processing, in particular, when high filler loading is used.⁹ All process oils include three complex components of aromatic, naphthenic, and paraffinic. Aromatic (C_A), naphthenic (C_N), and paraffinic (C_P) components contain more than one benzene ring, one cycloalkane ring substituted with aliphatic hydrocarbons, and only linear or branch aliphatic hydrocarbons, respectively. Generally, process oils are classified by the relative content of three components. As shown in Table 1, the aromatic content of process oil is increased with the order of paraffinic, MES, TDAE, and DAE. On the contrary, the paraffinic content is increased with the order of DAE, TDAE, MES, and paraffinic. Polyaromatic hydrocarbons (PAHs) included in aromatic components are defined as molecules having more than two aromatic rings composed of only carbon and hydrogen atoms. Polycyclic aromatics (PCAs) include much wider range than the former. This term covers molecules with different so-called heteroatoms such as sulfur, nitrogen, oxygen, and halogen. It is well known that PCAs are chrysene, benzo[a]pyrene, benzo[e]pyrene, benz[a]anthracene, 2,3-benzanthracene, benz[e]acetophen anthracene, dibenzo[a,j]anthracene, phenazine, thianthrene, benzofluoranthene[b,j,k], and etc. It was known that some PCAs cause skin cancer in mice.^{1,2,3} The PCA contents are increased with the order of paraffinic, MES, TDAE, and DAE, respectively.

FT-IR spectroscopy is a useful instrument to identify materials by infrared (IR) radiation. The IR spectra are obtained by vibration modes of materials. The vibration mode depends on

both bond strength (k) and the reduced mass (μ) of any material. Because all materials have their inherent k and μ , the characteristic spectra are obtained and materials can be identified. The expression for wavenumber can be described with eq. (1).

$$\sigma = 1/2\pi c (k/\mu)^{1/2} = 5.3 \times 10^{-12} (k/\mu)^{1/2} \quad (1)$$

Where σ is the wavenumber of an absorption peak in cm^{-1} , k is the force constant for the bond in dynes/cm, c is the velocity of light in cm/sec, and μ is the reduced mass.

Figure 1 shows the IR spectral patterns of standard oils. As previously described, TDAE, MES, and paraffinic oil belong to low PCA oil, meaning less than 3 wt% PCA. DAE belongs to high PCA oil, including more than 3 wt%. The spectra, as shown in Figures 1 (a), (b), (c), and (d) represent the characteristic absorption bands from a freshly made film of paraffinic, MES, TDAE, and DAE. The characteristic very weak absorption bands appearing at 1603 cm^{-1} resulted from the stretching vibration for double bond of aromatic ring. The absorption intensity of aromatic ring shows an increase with

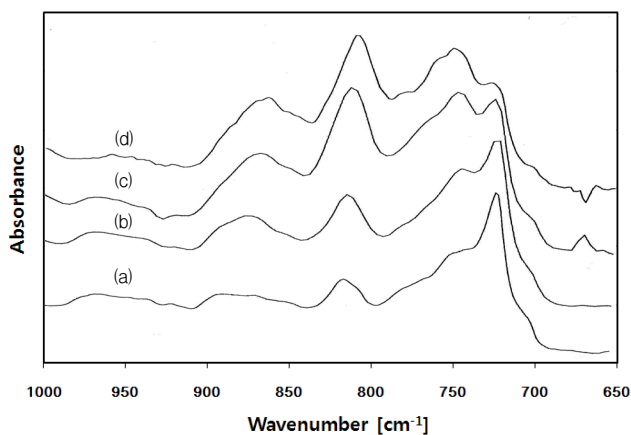


Figure 1. The FT-IR spectra of standard oils (a) Paraffinic, (b) Prorex 15 (MES), (b) Tyrex 20 (TDAE), and (d) Aromatic (DAE).

the order of paraffinic, MES, TDAE, and DAE, coinciding with aromatic content as shown in Table 1. Other characteristic absorption bands are shown at 864 , 810 , 754 , and 721 cm^{-1} . These bands can be used with great utility to identify PCA types among process oils, showing IR absorption by the substitution patterns of the aromatic ring and the pattern of paraffinic or naphthenic as summarized in Table 3. Most of PCAs are detected in these regions because they have various aromatic substituents. Table 4 shows the relative abundance of absorption peak calculated from each peak height based on baseline in Figure 1. Aromatic oil, a DAE type with a high PCA content as a potential carcinogene shows relatively high content at 810 cm^{-1} and 754 cm^{-1} . Tyrex 20, a TDAE type treated with hydrogenation or solvent extraction of DAE is classified as a non-carcinogen. This treated oil shows a small reduction in both 810 cm^{-1} and 754 cm^{-1} and an increase of 5% at 721 cm^{-1} , compared with DAE type. This may result in hydrotreating for 1,2-disubstituted or 1,2,3-trisubstituted aromatic ring. Prorex 15, known as a mild extract solvate (MES) contains lower aromatic content than DAE and TDAE. Because 85 wt% of this oil includes naphthenic or paraffinic components, the relative content at 721 cm^{-1} shows very high. Because paraffinic oil produced by vacuum distillate has the highest paraffin content, it shows the highest content at 721 cm^{-1} . As shown in Table 4, the relative content at 810 cm^{-1} shows a decrease with the order of DAE, TDAE, MES, and paraffinic. The relative content at 754 cm^{-1} shows almost the

Table 4. The Relative Abundance of Each Absorption Peak in Standard Oils

Process Oils	864 cm^{-1}	810 cm^{-1}	754 cm^{-1}	721 cm^{-1}
Aromatic	2.2 (13.9)	5.1 (32.2)	4.9 (30.6)	3.7 (23.3)
Tyrex 20	2.3 (13.9)	4.7 (28.5)	4.8 (29.1)	4.7 (28.5)
Prorex 15	1.6 (11.0)	2.9 (20.0)	4.4 (30.3)	5.6 (38.6)
Paraffinic	0.8 (6.8)	1.7 (14.5)	3.2 (27.4)	6.0 (51.3)

Numbers in parenthesis represent the relative abundance calculated from their peak heights based on baseline.

Table 3. The Characteristic FT-IR Peaks on Oil Components

Oil Componenets	FT-IR band, cm^{-1}	Materials
Aromatic	near 750	1,2-disubstituted
	near between 880 and 850	1,3-disubstituted
	near 880 and 810	1,2,3-trisubstituted
	near between 840 and 910	1,3,5-trisubstituted
	near 1600	double Bond of Aromatic Ring
Paraffinic or Naphthenic	near 723	-CH ₂ CH ₂ - rocking

same as about 30% in aromatic, TDAE, and MES but lower about 3% in paraffinic. The relative content at 721 cm^{-1} shows an increase with the order of DAE, TDAE, MES, and paraffinic. This table can be effectively used in determining PCA oil type from SBR vulcanizates.

2. Removal of Antidegradants from SBR Vulcanizates

Antidegradants in tire play an important role in protecting rubber oxidation from the outside or inside environment such as ozone, oxygen, ultraviolet ray, and heat.¹⁰ These rubber chemicals interrupt identification of oil type by FT-IR techniques because of IR absorption in the same region. HPPD shows IR absorption at wavenumber of 694 (weak), 748 (strong), 814 (peak), and 872 (very weak). It was identified that IR absorption peaks of HPPD at the wavenumber of 748, 810, and 872 overlapped with those of process oils. TMDQ shows IR absorption at wavenumber of 891 (very weak), 814 (strong), and 748 (strong). It was confirmed that IR absorption peaks of TMDQ at wavenumber of 748 and 810 overlapped with those of process oils. These chemicals must be effectively eliminated to identify PCA oil type.

To eliminate antidegradants from SBR vulcanizates, each sample was cut into 1 mm^3 in size. About 0.1 g of sample is weighted and extracted with 1.5 mL acetonitrile (ACN) in a vial at oven for 4 h. The qualitative and quantitative analysis of antidegradants was performed by GC. The retention time is the one reaching from injection to the peak and characteristic of these chemicals. The area produced for each peak is proportional to its concentration. Dibutyl phthalate (DBP) as the internal standard is used to determine the amount of antidegradants. After dissolving HPPD and TMDQ in raw with ACN, it was identified that the retention time of HPPD and TMDQ was 8.57 min and 11.24 min on chromatogram, respectively. It was known that extraction of antidegradants with ACN from SBR vulcanizate (S4) was independent of the effect of temperature because each peak area of HPPD and TMDQ in the extraction temperature of $40\text{ }^\circ\text{C}$, $60\text{ }^\circ\text{C}$, and $80\text{ }^\circ\text{C}$ for 4 h is almost the same. Therefore, all samples were extracted at $80\text{ }^\circ\text{C}$ oven for 4 h. Figure 2 shows the extracted materials from SBR vulcanizates by ACN. The extracted materials are HPPD (8.57 min), TMDQ (11.24 min), and a trace of oil by GC. These chemicals must be eliminated completely as described in the effect of temperature on extraction. Therefore, the effect on aromatic antidegradants such as HPPD and TMDQ of S1, S2, S3, S4, and S5 in determining oil type will be ignored.

3. Extraction of Oil and Wax from SBR Vulcanizates

The residual rubber which antidegradants were completely

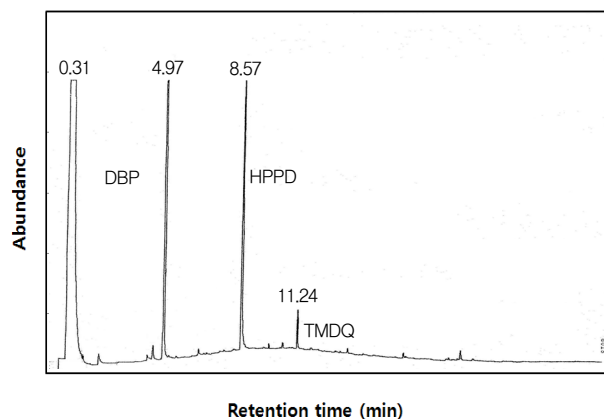


Figure 2. GC chromatogram of the extracts treated with ACN at $80\text{ }^\circ\text{C}$ for 4 h.

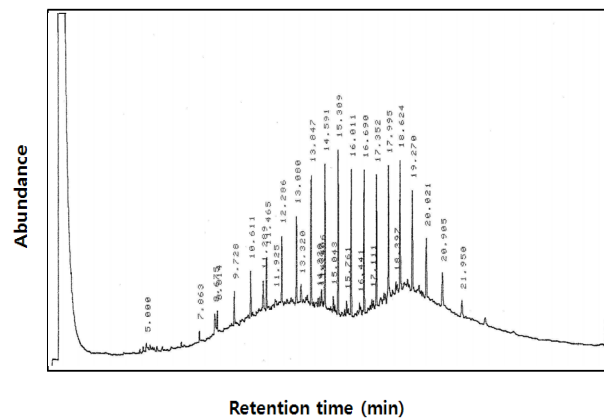


Figure 3. GC chromatogram of the extracts treated with *n*-hexane.

extracted in previous step was washed twice with ACN, dried, and dissolved in *n*-hexane to extract process oil. Figure 3 shows GC chromatogram after treating with *n*-hexane at $80\text{ }^\circ\text{C}$ oven for 4 h. This figure indicates that process oil and wax are effectively extracted. Process oil has various molecular weights ranging from 300 to 500, including complex mixtures of aromatic, naphthenic, and paraffinic. Therefore, GC curve for process oil shows a broad molecular weight distributions. Paraffin wax consists of linear or branched hydrocarbons containing carbon numbers ranging from 22 to 42. The peaks of wax in GC appear on oil curve in regular intervals according to one carbon number ($-\text{CH}_2-$). The maximum peak at 15.309 min was identified as carbon number 31.

4. Separation of Wax and Process Oil from *n*-hexane Extracts

The *n*-hexane extracts were dried to remove solvent at $80\text{ }^\circ\text{C}$

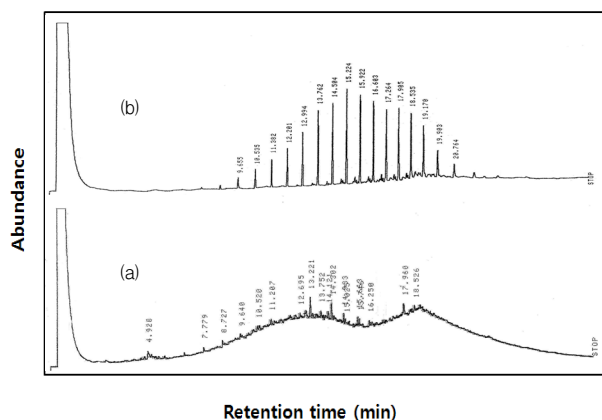


Figure 4. GC chromatogram of the extracts treated with cooling acetone ($-15\text{ }^{\circ}\text{C}$) (a) Purified Oil (yellowish liquid), and (b) Wax (white solid).

$^{\circ}\text{C}$ oven for 1h. Oil is a polar and high viscous liquid, whereas wax is nonpolar and white solid at room temperature because of higher molecular weight of hydrocarbons. Wax functions surface coating to protect rubber oxidation from ozone and ultraviolet in tire.¹¹ This chemical absorbs IR radiation at 721 cm^{-1} resulting in $-\text{CH}_2-\text{CH}_2-$ rocking, the same region with paraffinic or naphthenic. Because of this interference of wax in determining PCA oil type, wax from process oil must be eliminated completely. Fortunately, since solubility parameter and phase are very different each other, process oil can be separated effectively. To separate oil from *n*-hexane extracts, dried extracts were dissolved in acetone and performed in two temperature conditions. At room temperature, it was identified that a solution was separated with white precipitation and yellowish liquid. White precipitation was identified as wax of higher molecular weight including carbon numbers ranging from 29 to 42. A yellowish liquid was identified as process oil and part of low molecular of wax containing carbon numbers from 22 to 35. This partial separation maybe resulted in the similar physical properties between oil and lower molecular weight of wax. At lower temperature, $-15\text{ }^{\circ}\text{C}$, it is identified that wax from oil is effectively removed on GC chromatogram as shown in Figures 4 (a) and (b). Thus the purified oil is obtained to determine the type of PCA.

5. Determination of Low or High PCA on Purified Oil by FT-IR Spectroscopy

The purified oil from SBR vulcanizates in previous step was analyzed by FT-IR spectroscopy. PCA oil types were determined by the relative absorption intensity at 864 , 810 , 754 , and 721 cm^{-1} . The relative absorption intensity depends on the content of various aromatic components consisting of sub

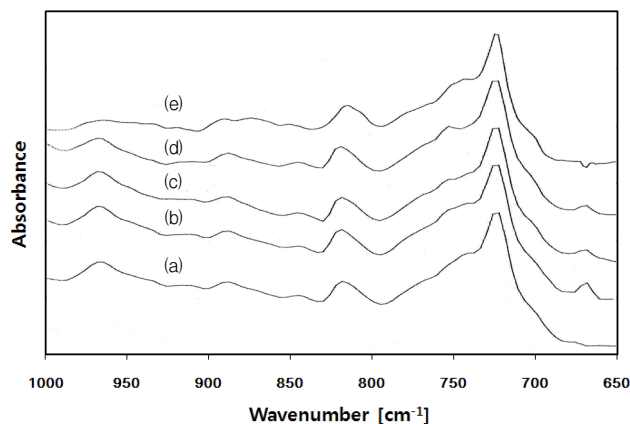


Figure 5. FT-IR spectra of the purified paraffinic oils from SBR vulcanizates (a) S1, (b) S2, (c) S3, (d) S4, and (e) S5.

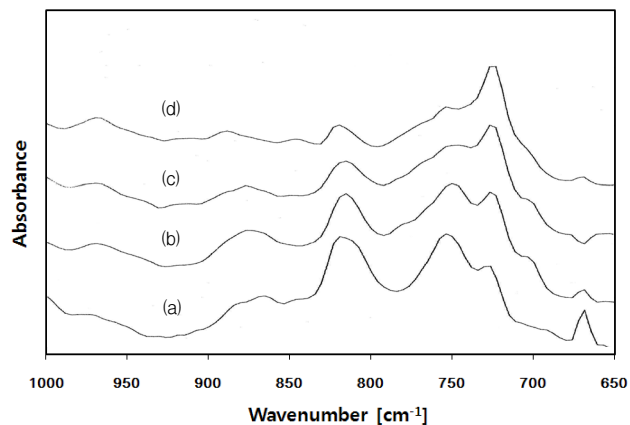


Figure 6. FT-IR spectra of the purified oil types from SBR vulcanizates (a) Aromatic (S6), (b) Tyrex 20 (S7), (c) Prorex 15 (S8), and (d) Paraffinic (S4).

stituted aromatic rings with or without heteroatoms such as S, N, O, and halogens as shown in Table 3. The absorption at 721 cm^{-1} shows the presence of paraffinic or naphthenic.

As shown in Figure 1, each of standard oils has its characteristic absorption pattern. We can easily and rapidly identify PCA oil type through coincidence of IR spectra of the purified and standard oil. Figures 5 (a), (b), (c), (d), and (e) show IR spectra of S1, S2, S3, S4, and S5, respectively. These figures show the effects of rubber chemicals such as wax, TMDQ, HPPD, TMDQ/HPPD, and processing aid like Structol 40MS. As previously described, rubber chemicals such as TMDQ, HPPD, and TMDQ/HPPD were completely extracted with ACN. The effects of rubber chemicals in determining oil type were ignored. Wax from oil was also eliminated with cooling acetone ($-15\text{ }^{\circ}\text{C}$). It is considered that processing aid having higher molecular weight distribution of hydrocarbons than that of process oil was not extracted from vulcanizates. Structol

Table 5. The Relative Abundance of Each Absorption Peak in the Purified Oil

Sample I.D.	864 cm ⁻¹	810 cm ⁻¹	754 cm ⁻¹	721 cm ⁻¹
S1	0.5 (4.9)	1.5 (14.6)	3.0 (29.1)	5.3 (51.9)
S2	0.5 (5.2)	1.3 (13.4)	2.7 (27.8)	5.2 (53.6)
S3	0.4 (4.1)	1.3 (13.3)	2.9 (29.3)	5.2 (53.1)
S4	0.4 (4.1)	1.4 (14.3)	2.7 (27.6)	5.3 (54.1)
S5	0.5 (5.0)	1.2 (12.0)	2.9 (29.0)	5.4 (54.0)
S6	2.8 (16.7)	5.2 (31.0)	5.0 (29.8)	3.8 (22.6)
S7	2.6 (14.1)	5.3 (28.6)	5.4 (29.2)	5.2 (28.1)
S8	1.6 (11.1)	2.9 (20.1)	4.4 (30.6)	5.5 (38.2)

Numbers in parenthesis represent the relative abundance calculated from their peak heights based on baseline.

40MS extracted by solvent from vulcanizates was difficult in analyzing by gas chromatograph because of strongly adhering to GC column. So, FT-IR spectroscopy is very useful to identify existence of processing aid. Like process oil, although processing aid such as Structol 40MS in raw absorbs near 870, 814, 748, and 721 cm⁻¹, it was confirmed that processing aid was not extracted from SBR vulcanizates by non-polar solvents such as toluene and *n*-hexane due to strong van der Waals force using FT-IR spectroscopy. Sample (S5) treated with ACN, *n*-hexane, and cooling acetone was analyzed by FT-IR spectroscopy. The FT-IR spectrum of S5 as shown in Figure 5 (e) shows the same result with S1, S2, S3, and S4, giving no effects on determination of PCA oil type through extraction processes with ACN, *n*-hexane, and cooling acetone. It was also considered that processing aid have no effect on determination of PCA oil type. Figure 6 shows the IR spectra on PCA oil types extracted from SBR vulcanizates. This indicates that the relative abundance of each absorption peak for the purified oils coincides well with that of standard oil. The relative abundance of each absorption peak calculated from Figure 5 and 6 is summarized in Table 5. Therefore, It can be possible to determine low or high PCA type becoming criteria of latent carcinogen for process oil used in tire tread.

IV. Conclusions

The purified oils from SBR vulcanizates were effectively

obtained through extraction and separation skills of acetonitrile, *n*-hexane, and then cooling acetone(-15 °C). Aromatic antidegradants such as HPPD, TMDQ, TMDQ/HPPD are effectively removed with ACN. After oil and wax are extracted from the residual rubber with *n*-hexane, wax from oil is effectively eliminated with cooling acetone (-15 °C). Extracts in all processes were identified by gas chromatograph. Whether low or high PCA oil for the purified oil based on happening oncogene was determined by FT-IR techniques. The identification of PCA oil type was determined by the relative abundance at the substitution patterns of aromatic ring and the pattern of paraffinic or naphthenic.

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