Research article

Comparison of polymeric components and tire wear particle contents in particulate matter collected at bus stop and college campus

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A B S T R A C T

Particulate matter ($PM_{2.5}$) samples were collected at two different places of a college campus (CC) and a bus stop (BS) nearby the college campus. The traffic volume of college campus was very low due to untact classes. Polymeric components and tire wear particle (TWP) contents in the $PM_{2.5}$ samples were analyzed using pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). Various polymeric components such as natural rubber (NR), bitumen, saturated hydrocarbons, poly(ethylene terephthalate) (PET), and plant-related particles (PRPs) were observed. NR and bitumen are key components of TWP of bus tire tread and asphalt pavement wear particle (APWP), respectively. The TWP contents in the $PM_{2.5}$ samples collected at the bus stop were larger than those collected at the college campus. For the same sampling site, the TWP content in the $PM_{2.5}$ sample collected for higher fine dust concentration in the air was greater than that for lower one. The $TWP_{2.5}$ concentration in the air for the BS sampling was higher than those for the CC sampling, even when the $PM_{2.5}$ concentration in the air for the former was lower than those for the latter. It can be concluded that the TWPs and APWPs in the $PM_{2.5}$ samples collected at the college campus should be transferred mostly from the outside road.

1. Introduction

Abrasion of tire tread, brake, and road is main source of traffic-related non-exhaust particulate matter (PM) [1–5]. Tire wear particles (TWPs) are produced by friction between the tire tread and the road surface. Some researchers reported that TWPs were less than 10% of PM_{10} and the amounts were depending on the driving conditions and places [6,7]. It was reported that contribution levels of urban $PM_{2.5}$ were traffic (25%), industrial activities (15%), domestic fuel burning (20%), unspecified sources of human origin (22%), and natural dust and salt (18%) [8]. Panko et al. analyzed $PM_{2.5}$ samples collected in London, Tokyo, and Los Angeles, and reported that TWP contribution in $PM_{2.5}$ was less than 1% [1].

Passengers waiting at a bus stop may be exposed to traffic-related PMs, which may lead to dire health outcomes such as cardio-vascular disease and respiratory effects [9–12]. There should be some difference in fine dust concentrations at the roadside and at a place far from the road and the TWP contents in the PM samples may be different according to the sampling places. In this study, $PM_{2.5}$ samples were collected at a college campus and a bus stop nearby the college campus. The sampling place in the college campus was front of the college museum. Because of COVID-19 pandemic, the traffic volume at the college campus was very low due to untact

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classes. The bus stop is located in the six-lane road and has 6 city bus lines. Kinds and concentrations of rubber in the $PM_{2.5}$ samples were analyzed, and the TWP contents were determined on the basis of the rubber analysis results and a reference rubber compound formulation.

Kinds of polymeric components in the $PM_{2.5}$ samples were analyzed using pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). Py-GC/MS has been widely used for analysis of polymeric materials including microplastics and rubber components in PMs [13–25]. Identification of polymeric materials using Py-GC/MS is performed by analysis of the principal pyrolysis produts. For example, principal pyrolysis produts of natural rubber (NR) are isoprene and dipentene, while those of styrene-butadiene rubber (SBR) are butadiene, styrene, and 4-vinylcyclohexene (VCH) [21,23–25]. Kinds of polymeric components in the PM samples collected on the impactor filter (PM_{IF}) were also examined, and they were compared with those of the $PM_{2.5}$ samples. Analysis results of the samples collected at college campus and bus stop were compared.

2. Materials and methods

2.1. Materials

Standard malysian rubber of SMR CV 60 was used as the reference natural rubber (NR). Toluene was purchased from Merck Co. (Germany). Ultra high purity grade helium (99.999%) was purchased from Daehan Special Gas Co. (Republic of Korea). Pyrofoil of 590 °C Curie temperature was purchased from Japan Analytical Industry Co. (Japan). PTFE filter of 46.2 mm was purchased from Hangzhou Anow Microfiltration Co. (China) and microglass fiber filter of 37 mm was purchased from Zefon International Inc. (USA).

2.2. Collection of $PM_{2.5}$

$PM_{2.5}$ samples were collected at two places of the bus stop nearby Sejong university in Seoul, Republic of Korea (37°32′59.0″N 127°04′32.3″E) and the front of Sejong university museum (37°33′05.0″N 127°04′30.4″E) (Fig. S1; Supplementary Information). The bus stop is located in the six-lane road and there are 6 city bus lines at the bus stop. The straight distance between the bus stop and the university museum is about 200 m. $PM_{2.5}$ sampling was carried out using a low volume particulate sampler of KMS-4200 (Kemik Co., Republic of Korea) and the 46.2 mm PTFE filter with a PP support ring. The 37 mm microglass fiber filter was employed as the impactor filter.

The $PM_{2.5}$ sampling was performed in the early spring (March) and in the early summer (June) of 2021 for 12 h/day during the day time from 7 a.m. to 7 p.m. The $PM_{2.5}$ sampling at the bus stop was performed on March 16–17 and June 14 and 16, 2021, while that at the college campus was carried out on March 29 and 30–31 and June 8–9, 2021. The total $PM_{2.5}$ sampling time was 24 h, except for the sampling at the college campus on March 29. On March 29, there was a fine dust warning and the $PM_{2.5}$ sampling was performed only for 9 h during severe fine dust concentration (Table S1; Supplementary Information). The sample codes were named as BS**** and CC**** for the bus stop and the college campus, respectively, and the '****' of four digits denotes the sampling date.

2.3. Analyses of SEM, EDS, and Py-GC/MS

The $PM_{2.5}$ samples were observed using a scanning electron microscope (CUBE-II tabletop SEM, Emcrafts Co., Republic of Korea). Element analysis of the $PM_{2.5}$ was performed by SEM-EDS analysis using Hitachi SU-8010 (Hitachi Co., Japan). The accelerating voltage was 15 kV and the resolution was 1.0 nm.

Py-GC/MS analysis was carried out using an Agilent 6890 gas chromatograph equipped with a 5973 mass spectrometer (Agilent Technology Inc., USA) equipped with a JCI-55 Curie point pyrolyzer (Japan Analytical Industry Co., Japan). A pyrofoil of 590 °C Curie temperature was used. Pyrolysis was performed for 10 s using the pyrofoil under helium (He) atmosphere. For the $PM_{2.5}$ samples, the filter collected $PM_{2.5}$ was punched with 10 mm of diameter and the three 10 mm samples were used for Py-GC/MS analysis (Fig. S2(a); Supplementary Information). For the PM_{IF} samples, the entire PM collected on the imfactor filterb was used for Py-GC/MS analysis (Fig. S2(b); Supplementary Information).

DB-5MS (30 m × 0.32 mm, film thickness 0.25 μm, Agilent Technology Inc., USA) was used. The sample inlet temperature was 250 °C, the split ratio was 1:15, and helium (1.8 mL/min) was used as the carrier gas. The GC oven temperature programming was as follows: 30 °C (held for 3 min) to 50 °C (held for 3 min) at a rate of 10 °C/min, to 180 °C (held for 1 min) at a rate of 10 °C/min, and then to 250 °C (held for 3 min) at a rate of 10 °C/min. The interface temperature of GC to MS was 250 °C. The electron ionization (70 eV) was used to ionize the pyrolysis products. The MS source temperature was 230 °C.

2.4. Quantification of NR concentrations in the $PM_{2.5}$

To build the calibration curve, 10.0 mg of SMR CV 60 was thoroughly dissolved in 5.0 mL of toluene. This NR solution was diluted to 1.0, 0.5, and 0.2 mg/mL. Each solution was dropped on the blank PTFE filter and the solvent was evaporated. The PTFE filter was cut 10 mm diameter using a round punch. The calibration sample preparation process was as follows: (1) fold a pyrofoil with U-shape, (2) place the 10 mm blank PTFE filter on the pyrofoil, (3) drop the NR solution of 5 μL on the center of the filter, and (4) evaporate the solvent in a convection oven at 70 °C for 30 min.

The NR samples of 1.0, 2.5, 5.0, and 10.0 μg were pyrolyzed for the calibration cuve. Calibration curve was plotted using the dipentene peak area. The $PM_{2.5}$-collected filter was cut 10 mm using the round punch. Three samples were analyzed and averaged. The

NR concentrations were determined using the calibration curve.

3. Results and discussion

3.1. Amounts of the collected PM samples

Amount of the $PM_{2.5}$ sample tended to be proportional to the fine dust concentration in the air (Tables S1 and S2; Supplementary Information). Amounts of the $PM_{2.5}$ samples collected at the bus stop were lower than those collected at the college campus because the fine dust concentrations during the sampling time at the bus stop were lower than those at the college campus. Amount of the $PM_{2.5}$ sample of CC0329 was lower than the others because of the short collection time. Amounts of the PM_{IF} samples were not related to the fine dust concentration in the air and did not show any specific trend.

3.2. SEM and EDS analyses of TWP in the $PM_{2.5}$ sample

The $PM_{2.5}$ samples were observed by SEM, and there were various particles (Fig. S3; Supplementary Information). Element analyses of two TWPs were carried out (Fig. S4 and Table S3; Supplementary Information). The most abundant element was fluorine (F) come from the PTFE filter. Most metal elements should originate from mineral particles. Besides the various metal elements, there were specific elements of sulfur (S) and zinc (Zn) come from elemental sulfur (S_8) and zinc oxide (ZnO) used as curatives of rubber vulcanizates, respectively. Tire tread compounds are crosslinked by sulfur cure system which usually contains elemental sulfur, sulfur cure accelerators, zinc oxide, and stearic acid [26–28]. By curing process, sulfur crosslinks between rubber chains are formed and zinc complexes are generated by reactions between zinc stearate and sulfur/sulfur cure accelerators [29,30]. Hence, extence of S and Zn is an important evidence of TWP. Carbon (C) source should be rubber of the TWP. The various metal components must be inorganic particles stuck into the TWP. In general, a TWP was found in the road as a form of tire-road wear particle (TRWP) composed of a TWP and a lot of inorganic particles [2,19].

3.3. Polymeric components in the $PM_{2.5}$ samples

Kinds of polymeric components in the $PM_{2.5}$ samples collected at the bus stop were identified by analysis of the pyrolysis products formed from the polymeric materials. Py-GC/MS chromatograms of the $PM_{2.5}$ samples collected at the bus stop were shown in Fig. 1. Pyrolysis products come from the PTFE filter in the chromatograms were almost not overlapped with other peaks, and their intensities were weak. The major pyrolysis products were summarized in Table 1. The principal pyrolysis products were dipentene, styrene, 1-alkenes, furfural, furan derivatives, acetophenone, and benzoic acid. Dipentene is the key pyrolysis product of NR (Scheme S1; Supplementary Information). Detection of dipentene is an important evidence that there is NR in the sample. The NR should come from bus TWPs because the tread rubber compounds of bus tires are mainly made of NR and the PM samples were collected at the bus stop [14,31–36].

Styrene can be generated from various polymeric components. Tread compounds of passenger car tires are mainly made of SBR. Styrene is the principal pyrolysis product of SBR along with 4-vinylcyclohexene (VCH) (Scheme S2; Supplementary Information) [23, 37–39]. Styrene was detected, but VCH was rarely observed. If there was SBR component in the $PM_{2.5}$ samples, besides styrene and VCH, 2-phenylpropene (2-PP), 3-phenylcyclopentene (3-PCP), and/or 4-phenylcyclohexene (4-PCH) should be detected because they are generated from the styrene-butadiene heterosequences [23,40,41]. However, 2-PP, 3-PCP, and 4-PCH were not detected. Hence, source of styrene was not SBR. Source of styrene may be bitumen used for asphalt pavement. Py-GC/MS chromatogram of bitumen
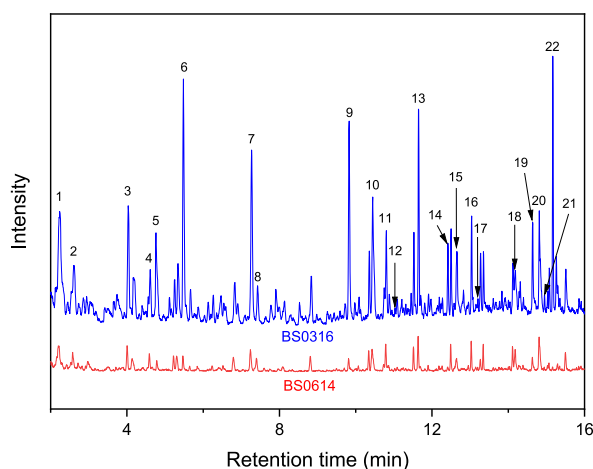

Fig. 1. Py-GC/MS chromatograms of $PM_{2.5}$ samples collected at the bus stop.

Table 1

Principal pyrolysis products of polymeric components in the $PM_{2.5}$ samples collected at the bus stop and their relative intensity ratios (the reference: dipentene).

Peak No.	Pyrolysis product	BS0316	BS0614
1	benzene	1.08 ± 0.32	1.02 ± 0.31
2	heptene	0.27 ± 0.04	0.43 ± 0.13
3	toluene	0.09 ± 0.12	1.04 ± 0.08
4	1-octene	0.25 ± 0.07	0.41 ± 0.07
5	n-octane	–	–
6	furfural	0.94 ± 0.59	0.46 ± 0.23
7	styrene	1.20 ± 0.27	0.97 ± 0.11
8	1-nonene	0.27 ± 0.06	0.40 ± 0.09
9	5-methyl-2-furancarboxyaldehyde	0.67 ± 0.54	0.35 ± 0.14
10	phenol	0.68 ± 0.28	0.66 ± 0.12
11	1-decene	0.34 ± 0.07	0.57 ± 0.18
12	n-decane	–	–
13	dipentene	1.00	1.00
14	acetophenone	0.23 ± 0.12	0.10 ± 0.04
15	4-methylphenol	0.45 ± 0.07	0.29 ± 0.04
16	1-undecene	0.35 ± 0.10	0.69 ± 0.15
17	n-undecane	0.06 ± 0.02	–
18	benzoic acid	0.21 ± 0.10	0.71 ± 0.22
19	naphthalene	0.46 ± 0.08	0.28 ± 0.06
20	1-dodecene	0.28 ± 0.02	0.33 ± 0.08
21	n-dodecane	0.04 ± 0.001	–
22	2,3-dihydrobenzofuran	0.92 ± 0.24	0.08 ± 0.09

clearly shows the styrene peak (Fig. S5(a); Supplementary Information). This implies that there were asphalt pavement wear particles (APWPs) in the PM samples.

Styrene might also come from polystyrene (PS) and poly(ethylene terephthalate) (PET) [42–45]. Besides styrene, acetophenone and benzoic acid are also principal pyrolysis products of PET [46,47]. Acetophenone and benzoic acid were detected in the $PM_{2.5}$ samples as listed in Table 1. This implies that there was PET component in the PM samples, and PET could come from lint of polyester (PET) fabric/clothes.

Alkenes (C_nH_{2n}) such as 1-heptene to 1-dodecene were observed in the $PM_{2.5}$ samples. But alkanes (C_nH_{2n+2}) such as n-octane to n-dodecane were rarely detected. Alkenes and alkanes are principal pyrolysis products of saturated hydrocarbons such as wax and polyethylene (PE). If it is PE, alkadienes must be detected as one of the principal pyrolysis products. But any alkadienes were not observed. Hence, there was no PE in the $PM_{2.5}$ samples. 1-Alkenes may be pyrolysis products of plant waxes [48]. In general, plant epicuticular wax is present in the surface layer of bark and leaf [49,50].

Furfural is one of key pyrolysis products formed from plant-related particles (PRPs) such as wood, bark, and leaves [51–53]. Wood particle was selected from the road dust collected at the bus stop, and it was pyrolyzed. Py-GC/MS chromatogram of the wood particle shows various pyrolysis products (Fig. S5(b); Supplementary Information). Besides furfural, 5-methyl-2-furancarboxyaldehyde, benzoic acid, and 2,3-dihydrobenzofuran were detected as the major pyrolysis products. Kinds and intensities of the pyrolysis products formed from PRPs are depending on the kinds and parts of plants.

The analysis results can be concluded that there were various polymeric components in the $PM_{2.5}$ samples such as TWPs, PRPs,
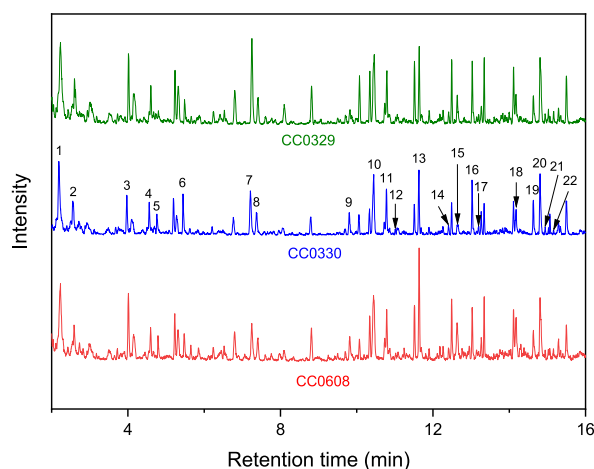

Fig. 2. Py-GC/MS chromatograms of $PM_{2.5}$ samples collected at the college campus.

APWPs (bitumen), and PET lint. The relative intensities of PRP-related pyrolysis products (furfural, 5-methyl-2-furancarboxyaldehyde, and 2,3-dihydrobenzofuran) and styrene in the BS0316 sample were greater than those in the BS0614 sample. This indicates that there were more PRPs and APWPs in the BS0316 sample than in the BS0614 sample.

Py-GC/MS chromatograms of the $PM_{2.5}$ samples collected at the bus stop were shown in Fig. 2, and the principal pyrolysis products were listed in Table 2. Like the $PM_{2.5}$ samples collected at the bus stop, there were various polymeric components and kinds of the pyrolysis products were nearly the same. The relative intensities of PRP-related pyrolysis products and styrene in the CC0329 sample were much greater than those in the CC0330 and CC0608 samples. This may be because the fine dust concentration in the air during the sampling time of the CC0329 sample was much greater than those of the others. The relative intensities of PRP-related pyrolysis products and styrene in the CC0330 sample were greater than those in the CC0608 sample. The relative intensities of PET-related pyrolysis products (acetophenone and benzoic acid) in the CC0329 sample were also much greater than those in the CC0330 and CC0608 samples.

The relative intensities of PRP-related pyrolysis products in the $PM_{2.5}$ samples collected in the early spring season were greater than those collected in the early summer season, irrespective of the sampling places. This may be because the early spring season is drier than the early summer season and there are more PRPs in the air during the early spring season than during the early summer season. The relative intensity of styrene in the CC0329 sample was much greater than those in the samples collected at the bus stop. This means that APWP source should be the outside because there was very low traffic volume in the college campus due to the COVID-19 pandemic.

Dipentene, styrene, and furfural could be used as the key markers of TWPs (NR), APWPs (bitumen), and PRPs, respectively. For the CC0329 sample, the average styrene/dipentene ratio was much greater than those of the others. This implies that there were a lot of APWPs in the CC0329 sample. Except for the CC0329 sample, the furfural/dipentene and styrene/dipentene ratios in the BS samples were relatively greater than those in the CC samples. The higher furfural/dipentene ratio in the BS samples could be explained by more plants surrounding the bus stop than the university museum (college campus). The relatively greater styrene/dipentene ratio in the BS samples might be because the bus stop is located closer to the road than the university museum.

3.4. Polymeric components in the PM_{IF} samples

Py-GC/MS chromatograms of the PM_{IF} samples collected at the bus stop were shown in Fig. 3(a), and the principal pyrolysis products were identified (Table S4; Supplementary Information). In the Py-GC/MS chromatograms, the dipentene and styrene peaks clearly appeared. This means that there were TWPs and APWPs in the PM_{IF} samples. But, the PRP-related pyrolysis products were rarely observed. The PET-related pyrolysis products such acetophenone and benzoic acid were also rarely observed.

Fig. 3(b) shows Py-GC/MS chromatograms of the PM_{IF} samples collected at the college campus, and the major pyrolysis products were identified (Table S5; Supplementary Information). In the Py-GC/MS chromatograms, the dipentene and styrene peaks were observed, but their relative intensities were smaller than those in the PM_{IF} samples collected at the bus stop. This implies that relative concentrations of TWPs and APWPs in the air at the college campus were lower than those at the bus stop. This is natural because the traffic volume was very low in the college campus due to the COVID-19 pandemic. The PRP-related pyrolysis products were not observed, except for furfural of the CC0608 sample. There was no specific trend of the styrene/dipentene ratios according to the

Table 2

Principal pyrolysis products of polymeric components in the $PM_{2.5}$ samples collected at the college campus and their relative intensity ratios (the reference: dipentene).

| Peak No.	Pyrolysis product	CC0329	CC0330	CC0608
1	benzene	2.20 ± 1.09	1.34 ± 0.35	0.90 ± 0.07
2	heptene	0.20 ± 0.04	0.42 ± 0.26	0.18 ± 0.05
3	toluene	1.84 ± 0.82	0.78 ± 0.18	0.81 ± 0.08
4	1-octene	0.44 ± 0.06	0.46 ± 0.25	0.23 ± 0.02
5	n-octane	–	–	–
6	furfural	0.72 ± 0.65	0.47 ± 0.31	0.38 ± 0.17
7	styrene	12.20 ± 6.58	1.10 ± 0.27	0.66 ± 0.11
8	1-nonene	0.60 ± 0.12	0.59 ± 0.24	0.29 ± 0.03
9	5-methyl-2-furancarboxyaldehyde	0.47 ± 0.45	0.38 ± 0.04	0.35 ± 0.12
10	phenol	0.74 ± 0.31	0.62 ± 0.09	0.63 ± 0.16
11	1-decene	0.73 ± 0.15	0.73 ± 0.28	0.35 ± 0.03
12	n-decane	–	–	–
13	dipentene	1.00	1.00	1.00
14	acetophenone	0.23 ± 0.18	0.12 ± 0.07	0.07 ± 0.02
15	4-methylphenol	0.35 ± 0.24	0.10 ± 0.08	0.47 ± 0.04
16	1-undecene	0.86 ± 0.27	0.73 ± 0.26	0.44 ± 0.01
17	n-undecane	0.08 ± 0.01	–	–
18	benzoic acid	0.65 ± 0.51	0.33 ± 0.12	0.43 ± 0.16
19	naphthalene	0.94 ± 0.77	0.38 ± 0.07	0.23 ± 0.06
20	1-dodecene	0.49 ± 0.38	0.34 ± 0.08	0.46 ± 0.35
21	n-dodecane	0.06 ± 0.01	–	–
22	2,3-dihydrobenzofuran	0.17 ± 0.10	0.06 ± 0.01	–
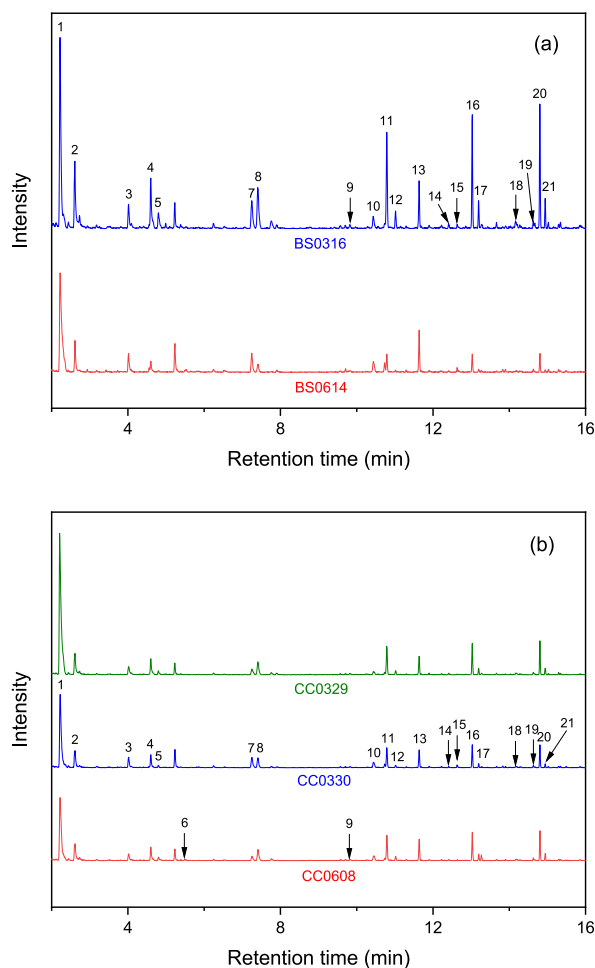
Fig. 3. Py-GC/MS chromatograms of PM_{IF} samples collected at the bus stop (a) and college campus (b).

sampling places. The interesting result was that the styrene/dipentene ratio for the CC0329 sample was the lowest although the styrene/dipentene ratio for its $PM_{2.5}$ sample was much greater than those for the other $PM_{2.5}$ samples. This may be due to difference in transferabilities of APWPs from the outside road to the college campus according to the APWP sizes. APWPs with the smaller size can transfer farther. This is another evidence that the source of APWPs collected at the college campus is mostly the outside road.

3.5. TWP contents in the $PM_{2.5}$ samples

The NR concentrations in the $PM_{2.5}$ samples were summarized in Table 3. The TWP content was determined using the reference tire tread compound formulation described at the bottom of Table 3. The reference NR compound formulation was determined based on the literature data [54–56]. In general, about 60 phr of carbon black is used for bus tire tread compounds. The other ingredients in the reference compound formulation include curatives (sulfur, zinc oxide, stearic acid, and sulfur cure accelerators), antidegradants, and processing aids. Since total weight of the reference compound formulation was 186 phr, the converting factor from the NR

Table 3
NR concentrations and estimated TWP contents in the $PM_{2.5}$ samples (wt%). Values in the parentheses were the NR concentrations of three 10 mm samples.

Sample code	NR concentration (wt%)	TWP content (wt%)*
BS0316	3.23 (4.22, 2.74, 2.73)	6.01
BS0614	1.96 (1.99, 1.94, 1.96)	3.65
CC0329	2.58 (2.56, 2.44, 2.73)	4.80
CC0330	1.08 (1.01, 1.13, 1.11)	2.01
CC0608	1.10 (1.07, 1.07, 1.15)	2.05

* Reference compound formulation (phr): NR (100), carbon black (60), other ingredients (26).

concentration to the TWP content was 1.86 (= 186/100). The TWP content in the BS0316 sample (6.0%) was greater than that in the BS0614 sample (3.7%). This can be explained by the fine dust concentrations in the air. The fine dust concentration in the air for the BS0316 sampling was greater than that for the BS0614 sampling (Table S1; Supplementary Information). Thus, it can be concluded that the difference in the TWP contents were closely related to the fine dust concentrations in the air.

The TWP content in the CC0329 sample (4.8%) was much greater than those in the CC0330 and CC0608 samples (2.0 and 2.1%, respectively), but it was lower than that in the BS0316 sample (6.0%) although the fine dust concentration in the air for the CC0329 sampling was much higher than that for the BS0316 sampling. Except for the CC0329 sample, the TWP contents in the BS samples were much greater than those in the CC samples though the fine dust concentrations in the air during the PM sampling at the bus stop were lower than those at the college campus. This implies that TWPs were much more present at the bus stop than in the college campus. The TWP content of the $PM_{2.5}$ samples collected at the college campus was over 2%. This is an intersting result since the sampling site in the college campus is far at least 20 m from the campus main road and the traffic volume was very small because of the COVID-19 pandemic. Hence, it can be concluded that the TWPs in the $PM_{2.5}$ samples collected at the college campus should originate from the outside road.

3.6. $TWP_{2.5}$ concentration in the air

Amounts of TWP in the $PM_{2.5}$ samples were calculated using weights of the $PM_{2.5}$ samples and the TWP contents in the $PM_{2.5}$ samples (Table 4). The TWP weight in the BS0316 sample was much larger than the other samples. This cannot be explained by the $PM_{2.5}$ concentration in the air because the $PM_{2.5}$ concentration during the BS0316 sampling was lower than those during the CC0330 and CC0608 sampling. This implies that there were fewer TWPs in the college campus due to very low traffic. The BS0316 sample contained larger amount of TWP than the BS0614 sample, and the $PM_{2.5}$ concentration in the air for the former was higher than that for the latter. Similarly, the CC0608 sample contained larger amount of TWP than the CC0330 sample, and the $PM_{2.5}$ concentration in the air for the former was higher than that for the latter. This means that in the same place the TWP content may tend to increase with the $PM_{2.5}$ concentration in the air.

Concentration of TWP with the size of smaller than 2.5 μm ($TWP_{2.5}$) in the air was calculated by dividing the sampling time into the amount of TWP in the $PM_{2.5}$ sample (Table 4). The $PM_{2.5}$ collection rate was 1.0 m^3/h. The $TWP_{2.5}$ concentration in the air for the CC0329 sampling was higher than those for the others due to the very high $PM_{2.5}$ concentration in the air. Although the $PM_{2.5}$ concentration in the air for the BS0316 sampling was lower than those for the CC0330 and CC0608 sampling, the $TWP_{2.5}$ concentration in the air for the BS0316 sampling was much higher than those for the CC0330 and CC0608 sampling. This implies that a lot of $TWP_{2.5}$ are flowed into the college campus from the outside road.

4. Conclusion

NR of TWPs, PRPs, bitumen of APWPs, and PET lint were found as the major polymeric components in the PM samples. Compositions and contents of the polymeric components varied depending on the PM samples ($PM_{2.5}$ and PM_{IF}) as well as the PM sampling places and times. PRPs were much more observed in the $PM_{2.5}$ samples than in the PM_{IF} samples. NR was detected in the PM samples as a rubber component, which implies that there were TWPs originated from abrasion of bus tire tread. The TWP contents were determined by the NR concentrations in the samples and the reference rubber compound formulation of bus tire treads. The TWP contents in the $PM_{2.5}$ samples collected at the bus stop (3.7 and 6.0%) were much greater than those collected at the college campus (2.0, 2.1, and 4.8%) due to the difference in the traffic volumes. The TWP content in the $PM_{2.5}$ sample collected at the college campus (4.8%) was high when the fine dust concentration in the air was very high (43 and 286 μg/m^3 for $PM_{2.5}$ and PM_{10}, respectively). The TWP content was dependent on the fine dust concentration in the air as well as the traffic volume. The $TWP_{2.5}$ concentration in the air for the BS sampling was much higher than those for the CC sampling, even when the $PM_{2.5}$ concentration in the air for the former was lower than those for the latter. Hence, it can be concluded that most sources of the TWPs and APWPs collected at the college campus were the outside road.

Author contribution statement

Eunji Chae: E. C.: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Sung-Seen Choi: Contributed reagents, materials, analysis tools or data; Wrote the paper.

Data availability statement

Data will be made available on request.

Funding

Table 4

Amounts of TWP in the PM$_{2.5}$ samples and the TWP$_{2.5}$ concentrations in the air.

Sample code	Amount of TWP (μg)	TWP$_{2.5}$ concentration (μg/m^3)
BS0316	30.05	1.25
BS0614	14.60	0.61
CC0329	14.40	1.60
CC0330	14.07	0.59
CC0608	16.40	0.68

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2023.e16558.

References

[1] J.M. Panko, K.M. Hitchcock, G.W. Fuller, D. Green, Evaluation of tire wear contribution to PM2.5 in urban environments, Atmosphere 10 (2019) 99.
[2] F. Sommer, V. Dietze, A. Baum, J. Sauer, S. Gilge, C. Maschowski, R. Gieré, Tire abrasion as a major source of microplastics in the environment, Aerosol Air Qual. Res. 8 (20181) 2014-2028.
[3] F. Amato, F.R. Cassee, H.A.C. Denier van der Gon, R. Gehrig, M. Gustafsson, W. Hafner, R.M. Harrison, M. Jozwicka, F.J. Kelly, T. Moreno, A.S.H. Prevot, M. Schaap, J. Sunyer, X. Querol, Urban air quality: the challenge of traffic non-exhaust emissions, J. Hazard Mater. 275 (2014) 31–36.
[4] M. Dall'Osto, D.C.S. Beddows, J.K. Gietl, O.A. Olatunbosun, X. Yang, R.M. Harrison, Characteristics of tyre dust in polluted air: studies by single particle mass spectrometry (ATOFMS), Atmos. Environ. 94 (2014) 224–230.
[5] H. Denier van der Gon, M.E. Gerlofs-Nijland, R. Gehrig, M. Gustafsson, N. Janssen, R.M. Harrison, J. Hulskotte, C. Johansson, M. Jozwicka, M. Keuken, K. Krijgsheld, L. Ntziachristos, M. Riediker, F.R. Cassee, The policy relevance of wear emissions from road transport, now and in the future - an international workshop report and consensus statement, J. Air Waste Manag. Assoc. 63 (2012) 136–149.
[6] J. Kwak, H. Kim, J. Lee, S. Lee, Characterization of non-exhaust coarse and fine particles from on-road driving and laboratory measurements, Sci. Total Environ. 458–460 (2013) 273–282.
[7] R. Gehrig, M. Hill, B. Buchmann, D. Imhof, E. Weingartner, U. Baltensperger, PM10 emissions of road traffic from abrasion and resuspension processes, in: Paper presented at PM and emission inventories scientific workshop, 2004. Milan, Italy.
[8] F. Karagulian, C.A. Belis, C.F.C. Dora, A.M. Prüss-Ustün, S. Bonjour, H. Adair-Rohani, M. Amann, Contributions to cities' ambient particulate matter (PM): a systematic review of local source contributions at global level, Atmos. Environ. 120 (2015) 475–483.
[9] L.T.N. Ngoc, M. Kim, V.K.H. Bui, D. Park, Y.-C. Lee, Particulate matter exposure of passengers at bus stations: a review, Int. J. Environ. Res. Publ. Health 15 (2018) 2886.
[10] A. Moore, M.A. Figliozzi, Statistical study of variables associated with particulate matter exposure levels at bus shelters, Transport. Res. Rec. 2341 (2013) 83–90.
[11] A. Moore, M.A. Figliozzi, C.M. Monsere, Air quality at bus stops: empirical analysis of exposure to particulate matter at bus stop shelters, Transport. Res. Rec. 2270 (2012) 76–86.
[12] D.B. Hess, P.D. Ray, A.E. Stinson, J.Y. Park, Determinants of exposure to fine particulate matter (PM2.5) for waiting passengers at bus stops, Atmos. Environ. 44 (2010) 5174–5182.
[13] J.V. Miller, J.R. Maskrey, K. Chan, K.M. Unice, Pyrolysis-gas chromatography- mass spectrometry (Py-GC-MS) quantification of tire and road wear particles (TRWP) in environmental matrices: assessing the importance of microstructure in instrument calibration protocols, Anal. Lett. 55 (2022) 1004–1016.
[14] E. Chae, U. Jung, S.-S. Choi, Quantification of tire tread wear particles in microparticles produced on the road using oleamide as a novel marker, Environ. Pollut. 288 (2021), 117811.
[15] E. Chae, S.-S. Choi, Building calibration curve for Py-GC/MS analysis of SBR/BR blend rubber compounds, Elast. Compos. 55 (2020) 281–288.
[16] S. Fischer, M. Fischer, C. Lorenz, G. Gerdts, B.M. Scholz-Böttcher, Comparison of pyrolysis gas chromatography/mass spectrometry and hyperspectral FTIR imaging spectroscopy for the analysis of microplastics, Anal. Bioanal. Chem. 412 (2020) 8283–8298.
[17] P. Eisentraut, E. Dumichen, A. Sebastian Ruhl, M. Jekel, M. Albrecht, M. Gehde, U. Braun, Two birds with one stone-fast and simultaneous analysis of microplastics: microplastics derived from thermoplastics and tire wear, Environ. Sci. Technol. Lett. 5 (2018) 608–613.
[18] T. Lachowicz, J. Zieba-Palus, P. Koscielniak, Pyrolysis gas chromatography- mass spectrometry for the characterization of tire marks for forensic analysis, Anal. Lett. 47 (2014) 1107–1117.
[19] K.M. Unice, M.L. Kreider, J.M. Panko, Comparison of tire and road wear particle concentrations in sediment for watersheds in France, Japan, and United Sates by quantitative pyrolysis GC/MS analysis, Environ. Sci. Technol. 47 (2013) 8138–8147.
[20] K.M. Unice, M.L. Kreider, J.M. Panko, Use of a deuterated internal standard with pyrolysis-GC/MS dimeric marker analysis to quantify tire tread particles in the environment, Int. J. Environ. Res. Publ. Health 9 (2012) 4033–4055.
[21] S.-S. Choi, J.-E. Ko, Influence of thermal aging on pyrolysis pattern of carbon black-filled NR composite, Macromol. Res. 15 (2007) 482–485.
[22] G. Sarkissian, J. Keegan, E. Du Pasquier, J.-P. Depriester, P. Rousselot, The analysis of tires and tire traces using FTIR and Py-GC/MS, J. Can. Soc. Forens. Sci. 37 (2004) 19–37.
[23] S.-S. Choi, Characteristics of pyrolysis pattern of styrene-butadiene rubbers with differing microstructures, J. Anal. Appl. Pyrolysis 62 (2002) 319–330.
[24] S.R. Shield, G.N. Ghebremeskel, C. Hendrix, Pyrolysis-GC/MS and TGA as tools for characterizing blends of SBR and NBR, Rubber Chem. Technol. 74 (2001) 803–813.
[25] S.-S. Choi, Correlation of crosslink density with pyrolysis pattern of natural rubber vulcanizates with efficient vulcanizing cure system, J. Anal. Appl. Pyrolysis 52 (1999) 105–112.
[26] J. Seo, W. Kim, S. Bae, J. Kim, Influence of loading procedure of liquid butadiene rubber on properties of silica-filled tire tread compounds, Elast. Compos. 57 (2022) 129–137.
[27] G. Ryu, D. Kim, S. Song, K. Hwang, W. Kim, Effect of molecular weight of epoxidized liquid isoprene rubber as a processing aid on the vulcanizate structure of silica filled NR compounds, Elast. Compos. 56 (2021) 223–233.

[28] G. Ryu, D. Kim, S. Song, H.H. Lee, J.U. Ha, W. Kim, Wear particulate matters and physical properties of ENR/BR tread compounds with different ratio of silica and carbon black binary filler systems, Elast. Compos. 56 (2021) 234–242.

[29] P. Junkong, R. Morimoto, K. Miyaji, A. Tohsan, Y. Sakaki, Y. Ikeda, Effect of fatty acids on the accelerated sulfur vulcanization of rubber by active zinc/carboxylate complexes, RSC Adv. 10 (2020) 4772.

[30] H. Kato, F. Nakatsubo, K. Abe, H. Yano, Crosslinking via sulfur vulcanization of natural rubber and cellulose nanofibers incorporating unsaturated fatty acids, RSC Adv. 5 (2015), 29814.

[31] S.-S. Choi, S.R. Yang, E. Chae, C.E. Son, Influence of carbon black contents and rubber compositions on formation of wear debris of rubber vulcanizates, Elast. Compos. 55 (2020) 108–113.

[32] C. Sirisinha, P. Sae-oui, K. Suchiva, P. Thaptong, Properties of tire tread compounds based on functionalized styrene butadiene rubber and functionalized natural rubber, J. Appl. Polym. Sci. 137 (2020), 48696.

[33] T. Miyazaki, Rubber Composition, European Patent, 2017, p. EP3459996.

[34] M.H.R. Ghoreishy, M. Alimardani, R.Z. Mehrabian, S.T. Gangali, Modeling the hyperviscoelastic behavior of a tire tread compound reinforced by silica and carbon black, J. Appl. Polym. Sci. 128 (2013) 1725–1731.

[35] H.M. Kim, C.-S. Lee, A study on noise resistance and physical properties of NBR rubber materials containing oleamide and aramid chip, Elast. Compos. 41 (2006) 79–87.

[36] S. Schaal, M. Martin, L. Migliarini, Tyre Having a High Wear Resistance, Tread Band and Elastomeric Compposition Used Therein, US Patent US 2005O234165, 2005.

[37] S.-S. Choi, H.-M. Kwon, Considering factors on determination of microstructures of SBR vulcanizates using pyrolytic analysis, Polym. Test. 89 (2020), 106572.

[38] S.-S. Choi, Influence of silane coupling agent on pyrolysis pattern of styrene- butadiene rubber in filled rubber compounds, Bull. Kor. Chem. Soc. 22 (2001) 1145–1148.

[39] S.-S. Choi, Characterization of bound rubber of filled styrene-butadiene rubber compounds using pyrolysis-gas chromatography, J. Anal. Appl. Pyrolysis 55 (2000) 161–170.

[40] S.-S. Choi, H.-M. Kwon, Analytical method for determination of microstructures of solution styrene-butadiene copolymers using 2-phenylpropene/styrene ratio of pyrolysis products, Polym. Test. 44 (2015) 153–159.

[41] S.-S. Choi, H.-M. Kwon, Characterization of pyrolysis products formed from styrene-1,2-unit heterosequence of styrene-butadiene copolymer, J. Anal. Appl. Pyrolysis 99 (2013) 1–8.

[42] S. Kumagai, R. Yamasaki, T. Kameda, Y. Saito, A. Watanabe, C. Watanabe, N. Teramae, T. Yoshioka, Catalytic pyrolysis of poly(ethylene terephthalate) in the presence of metal oxides for aromatic hydrocarbon recovery using tandem μ-reactor-GC/MS, Energy Fuels 34 (2020) 2492–2500.

[43] E.J. Dziwinski, J. Ilowska, J. Gniady, Py-GC/MS analyses of poly(ethylene terephthalate) film without and with the presence of tetramethylammonium acetate reagent, Comparative study, Polym. Test. 65 (2018) 111–115.

[44] N. Dimitrov, L.K. Krehula, A.P. Sirocic, Z. Hrnjak-Murgic, Analysis of recycled PET bottles products by pyrolysis-gas chromatography, Polym. Degrad. Stabil. 98 (2013) 972–979.

[45] A. Karaduman, Pyrolysis of polystyrene plastic wastes with some organic compounds for enhancing styrene yield, Energy Sources 24 (2002) 667–674.

[46] A. Dhahak, G. Hild, M. Rouaud, G. Mauviel, V. Burkle-Vitzthum, Slow pyrolysis of polyethylene terephthalate: online monitoring of gas production and quantitative analysis of waxy products, J. Anal. Appl. Pyrolysis 142 (2019), 104664.

[47] T. Yoshioka, G. Grause, C. Eger, W. Kaminsky, A. Okuwaki, Pyrolysis of poly(ethylene terephthalate) in a fluidised bed plant, Polym. Degrad. Stabil. 86 (2004) 499–504.

[48] E. Chae, S.-S. Choi, Analysis of polymeric components in particulate matter using pyrolysis-gas chromatography/mass spectrometry, Polymers 14 (2022) 3122.

[49] J. Weber, L. Schwark, Epicuticular wax lipid composition of endemic European Betula species in a simulated ontogenetic/diagenetic continuum and its application to chemotaxonomy and paleobotany, Sci. Total Environ. 730 (2020), 138324.

[50] Q. Liu, P. Liu, Z.-X. Xu, Z.-X. He, Q. Wang, Bio-fuel oil characteristic of rice bran wax pyrolysis, Renew. Energy 119 (2018) 193–202.

[51] S.-S. Choi, M.-C. Kim, Y.-K. Kim, Formation of methoxybenzenes from cellulose in the presence of tetramethylammonium hydroxide by pyrolysis, Bull. Kor. Chem. Soc. 34 (2013) 649–652.

[52] S.-S. Choi, M.-C. Kim, Y.-K. Kim, Influence of silica on formation of levoglucosan from carbohydrates by pyrolysis, J. Anal. Appl. Pyrolysis 90 (2011) 56–62.

[53] T. Lojewski, T. Sawoszczuk, J.M. Lagan, K. Zieba, A. Baranski, J. Lojewska, Furfural as a marker of cellulose degradation. A quantitative approach, Appl. Phys. A 100 (2010) 873.

[54] E. Chae, U. Jung, S.-S. Choi, Quantification of tire tread wear particles in microparticles produced on the road using oleamide as a novel marker, Environ. Pollut. 288 (2021), 117811.

[55] S.-S. Choi, S.R. Yang, E. Chae, C.E. Son, Influence of carbon black contents and rubber compositions on formation of wear debris of rubber vulcanizates, Elast. Compos. 55 (2020) 108–113.

[56] M.H.R. Ghoreishy, M. Alimardani, R.Z. Mehrabian, S.T. Gangali, Modeling the hyperviscoelastic behavior of a tire tread compound reinforced by silica and carbon black, J. Appl. Polym. Sci. 128 (2013) 1725–1731.