

DETERMINATION OF STYRENE-BUTADIENE AND ISOPRENE TIRE TREAD RUBBERS IN PILED PARTICULATE MATTER

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ABSTRACT

A method of simply and quickly determining styrene-butadiene (SBR) and isoprene (NR) tire tread rubbers in piled particulate matter on a highway was investigated.

The particulate matter was analyzed with a gas chromatograph to which a Curie-point pyrolyzer was attached. The contents of the SBR and NR tire tread rubbers in the piled particulate matter were determined by measuring the generated amount of styrene and dipentene (1-methyl-4-isopropylcyclohexene) attributed to the respective rubber polymers contained in the matter, and the calibration curves of the amounts of the standard tire tread rubbers plotted against the peak areas of styrene and dipentene generated by the pyrolysis. The pyrolysis of the rubber polymers was conducted at 590°C for 5 seconds.

The average contents of SBR tire tread rubber in piled particulate matter collected on the inside and outside of a tunnel on the highway were 0.0675-0.0920 and 0-0.0653 wt.%, respectively, and those of NR tire tread rubber were 0.127-0.176 and 0-0.100 wt.%.

Gas chromatography; isoprene; polymers; pyrolysis; rubber, isoprene; rubber, styrene-butadiene; styrene-butadiene; tires.

INTRODUCTION

It is generally thought that tire tread rubber particles, generated when car tires are abraded, are a latent pollutant which may tend to cause environmental contamination. Dannis has estimated that the average abrasion ratio of rubber used in one car tire was 90 mg/km [1]. The rubbers used in the tire treads of motor cars are styrene-butadiene rubber (SBR) types containing various additives and a small amount of BR, and isoprene rubber (NR) types containing additives and a small amount of SBR. The SBR are generally used in the tire treads of passenger cars, and the NR in the relatively large-sized tires of buses, trucks, and the like. The additives include carbon black, process oil (aromatics), and so forth, which contain

carcinogenic polycyclic aromatic hydrocarbons [2-5]. In view of this, it is more important to monitor the particles of tire tread rubbers as an environmental pollutant.

Some reports have been found on determination of tire tread rubbers contained in piled particulate matter [6-9]. However, most of the analytical methods described in the reports are unsuitable for simultaneous determination of SBR and NR, because the methods employ different separation conditions for pyrolyzates of SBR and NR which are subjected to gas chromatographic (GC) analysis.

In this investigation, in order to achieve the simultaneous determination of SBR and NR, we examined the selection of those pyrolyzates which are useful as an index for the determination of the rubber polymers, and the separation conditions for the pyrolyzates, in order that they may be subjected to GC analysis. The results of the investigation were satisfactory. Moreover, this method was applied to the determination of the contents of SBR and NR tire tread rubber particles in piled particulate matter collected at the inside and outside of a tunnel on a highway roadside.

EXPERIMENTAL

Materials

The standard SBR and NR tire tread rubber samples used in the experiment were cured rubber sheets of about 2 mm thickness, which were supplied by Yokohama Rubber Co. These rubbers were of the same type as the rubbers used in the tire treads of general economy cars. The sheet-shaped rubbers were ground with a grinder to provide powder for the experiment.

Apparatus and GC conditions

A Curie-point pyrolyzer (Model JHP-2, Japan Analytical Industry Co.) was coupled directly to a gas chromatograph (Model GC-8APF, Shimadzu) equipped with a flame ionization detector, which can be equipped either with a packed column or a capillary column.

For the packed column, a 3 m X 3 mm I.D. glass column containing 20% silicone DC 710 on Diasolid M (60-80 mesh) (Gasukuro Kogyo Co.) was used. The oven temperature was 165°C. The temperatures of injection and detection ports were both 190 °C. The carrier gas used was nitrogen and the flow-rate was 30 ml/min.

For the capillary column, a 25 mX0.2 mm I.D. fused silica capillary column coated with 5% phenylmethylsilicone (HiCap-CBP5, Shimadzu) was used. The column temperature was increased from 60°C to 150°C at a programme rate of 5°C/min. The temperatures of the injection and detec-

tion ports were both 190°C. The carried gas used was helium and the flow-rate was 0.87 ml/min with a splitting ratio of 1 : 60.

The peak areas of the pyrolyzates were measured by an integrator (Model C-R3A, Shimadzu).

Procedure

For piled particulate matter samples, piled paniculate matter present on the surface of 30 cm X 30 cm square at the side of a paved highway were collected, and were sieved through a 28-mesh sieve so that large particles were removed, and then dried in a desiccator. Amounts of less than 1 mg of the dried piled particulate matter samples were weighed out with a microbalance (Mettler), and were placed directly on pyrofoil, and then subjected to pyrolysis-GC analysis.

The contents of the SBR and NR tire tread rubbers were determined by pyrolyzing the piled particulate matter samples and measuring the amounts of styrene and dipentene produced, and then using the respective calibration curve. However, the NR tire tread rubber contained a small amount of SBR rubber from which styrene was generated. This would cause an error in the measured content of the SBR tire tread rubber. Accordingly, firstly, the amount of dipentene generated was used to calculate the content of the NR tire tread rubber in the sample. Then the amount of styrene attributed to the NR tire tread rubber and contained in the sample was estimated. From the amount of styrene produced by the pyrolysis of the sample, the estimated amount of styrene was subtracted. By using the difference between the amounts of styrene, the content of the SBR tire tread rubber in the sample was calculated.

RESULTS AND DISCUSSION

Pyrolyzates

Fig. 1 shows the pyrograms of the piled paniculate matter sample which was analyzed by pyrolysis-GC with a packed column and a capillary column. The pyrolysis temperature was 590-C, and the time was 5 s. The peaks of the pyrolyzates were identified by comparing the retention times of the standard substances.

The pyrolyzates obtained by the pyrolysis of the SBR tire tread rubber were butadiene, styrene, benzene, etc., the main pyrolyzates being butadiene and styrene. In the pyrograms, the styrene peak is apparently separated, but that of butadiene is insufficiently separated, overlapping the peak of an unknown substance. Therefore, this study employed the peak of styrene as an index for determination of the content of SBR tire tread rubber in a piled particulate matter sample.

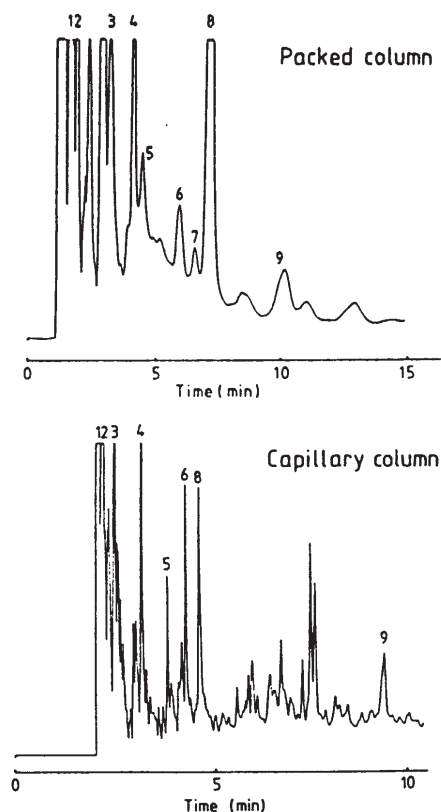


Fig. 1. Pyrograms of piled particulate matter samples on the highway. Peaks: 1 = butadiene, 2 = isoprene, 3 = benzene, 4 = toluene, 5 = vinylcyclohexane, 6 = ethylbenzene, 7 = xylene, 8 = styrene, 9 = dipentene.

On the other hand, the pyrolysis of the NR tire tread rubber gave isoprene, a main component of the NR rubber, and dipentene, the dimer (cyclization) of isoprene [10-12]. Furthermore, the pyrolysis gave styrene, benzene, toluene, and the like which might be attributed to used SBR, process oil and so forth. As an index for use in the determination of the NR tire tread rubber, the dipentene peak was used, because the amount of dipentene could be determined simultaneously with that of styrene under the same GC conditions, and the peak of dipentene in the pyrogram was clearly separated from other peaks.

Pyrolysis temperature

The correlation between the pyrolysis temperature and the pyrolyzates of the standard SBR and NR tire tread rubber samples was examined. Fig. 2 shows the results. The comparison of the yields of styrene generated by pyrolyzing the standard SBR tire tread rubber sample at six different

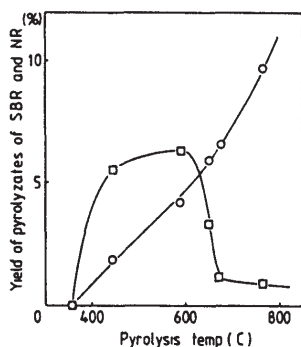


Fig 2 Relationship between the pyrolysis temperature and the yield of characteristic pyrolyzates of SBR and NR tire tread rubbers ○ = Styrene □ = dipentene

pyrolysis temperatures revealed that the styrene yield increased linearly with the pyrolysis temperature; For the standard NR tire tread rubber sample, the pyrolysis at about 450-600°C gave a maximum yield of dipentene. The reason seems to be that, above a pyrolysis temperature of 600°C there was an increase in the amount of the pyrolyzates such as isoprene and low molecular weight hydrocarbons.

We selected 590°C as the most reasonable pyrolysis temperature at which styrene and dipentene were generated at relatively high yields. Under such conditions the yields of styrene and dipentene were about 4.5 and 6.0 wt.% respectively.

Pyrolysis time

The effect of the pyrolysis time on the yield of styrene and dipentene was examined next. Fig. 3 shows the correlation between the yields of styrene and dipentene and the pyrolysis time. When the standard SBR tire tread rubber sample was pyrolyzed at 590°C, the yield of styrene was constant with a pyrolysis time of 4 seconds and longer. With a pyrolysis time of

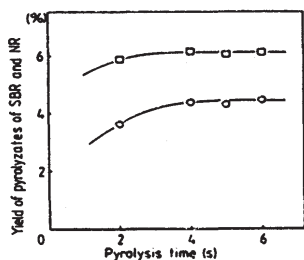


Fig. 3. Relationship between the pyrolysis time and the yield of characteristic pyrolyzates of SBR and NR tire tread rubbers. ○ = Styrene, □ = dipentene.

shorter than 4 seconds, the yield of styrene decreased as the pyrolysis time decreased. For the standard NR tire tread rubber sample, the same tendency as described above was found.

Calibration curves

It is very difficult to determine the content of SBR and NR tire tread rubbers in piled particulate matter with high accuracy, because various commercial tire tread rubbers with different compositions are used.

Fig. 4 demonstrates two calibration curves which show the correlation between the amounts of the standard tire tread rubber samples and the peak areas of styrene and dipentene attributed to the respective rubber polymers.

The relation between the amounts of the standard SBR and NR tire tread rubber samples subjected to pyrolysis-GC analysis and the yields of styrene and dipentene attributed to the respective polymers was examined. As a result, it was confirmed that constant yields were obtained for styrene and dipentene when the amounts of the standard SBR and NR rubber samples were below 5 and 1 mg, respectively.

For estimation of the content of SBR in the standard NR tire treadrubber sample, this sample was pyrolyzed at 590°C for 5 seconds. The peak area of the resultant styrene and the above mentioned calibration curve of SBR were used to determine the amount of SBR contained in the NR tire tread rubber sample. The average concentration of SBR obtained by 13 repeated measurements was 6.1 wt.%.

Therefore, for determination of the content of SBR tire tread rubber in a piled particulate matter sample, 6.1 wt.% of the weight of NR tire tread

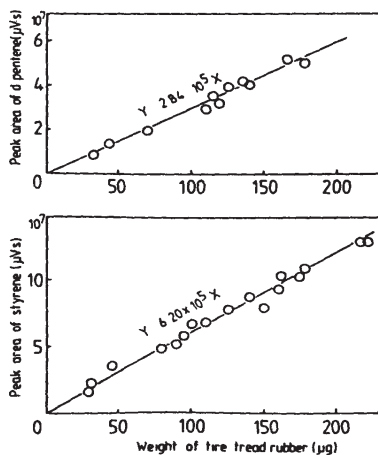


Fig 4 Calibration curves for (bottom) SBR and (top) NR tire tread rubbers

rubber determined by the pyrolysis-GC analysis should be subtracted from the weight of the SBR tire tread rubber determined by the pyrolysis-GC analysis.

Applications

The content of tire tread rubbers in piled particulate matter collected on the inside, at the entrance and on the outside of a tunnel on a paved highway of Route 246 on the roadside (Kanagawa Prefecture, Japan), was measured in July, 1985 (Fig. 5). The average contents of SBR tire tread rubber in the piled particulate matter samples taken at distances of 60 m and 20 m inside the tunnel, at the entrance, and at 20 m and 30 m outside were 0.0920, 0.0675, 0.0630, 0.0554, and 0.0100 wt.%, respectively. The average contents of NR tire tread rubber at the same sites were 0.176, 0.162, 0.148, 0.0140, and 0.0085 wt.%. The contents of SBR tire tread rubber measured at distances of 10 m and 20 m from the entrance of the tunnel in the direction perpendicular to the highway were 0.058 and 0.0075 wt.%, respectively. The contents of NR tire tread rubber at the same sites were 0.082 wt.%, and a trace amount. At distances of 30 m and longer from the entrance of the tunnel, neither SBR nor NR rubber was detected. The result suggests that the particles of SBR and NR tire tread rubbers generated by

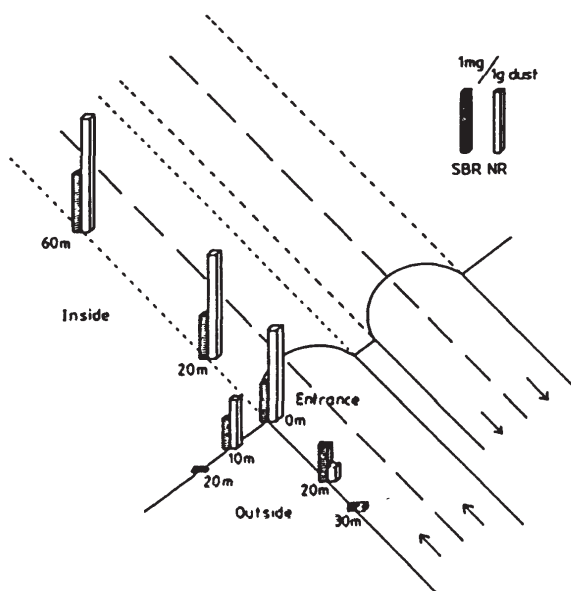


Fig. 5. Contents of SBR and NR tire tread rubbers in piled particulate matter on the highway (Route 246 highway, Kanagawa, Japan).

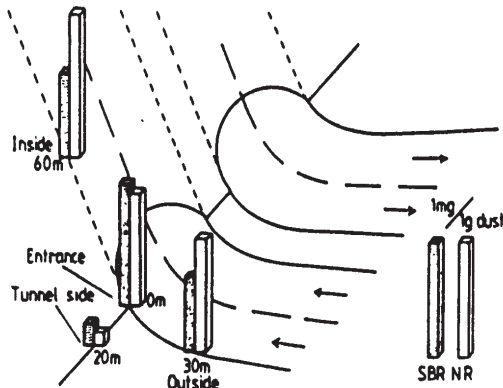


Fig. 6. Contents of SBR and NR tire tread rubbers in piled particulate matter (Route 246 highway, Kanagawa, Japan).

abrasion of car tires tended to accumulate to a relatively high degree on the inside of the tunnel, which was scarcely directly influenced by climate or weather conditions outside the tunnel.

Fig. 6 shows the contents of SBR and NR tire tread rubbers collected at different positions from the above measurement sites. The contents of SBR tire tread rubber at the inside of the tunnel, 60 m from the entrance, at the entrance, and at 30 m from the outside of the tunnel were 0.0764, 0.105, and 0.0653 wt.%, respectively. The contents of NR tire tread rubber at these sites were 0.127, 0.100, and 0.100 wt.%. In this case, the content of SBR tire tread

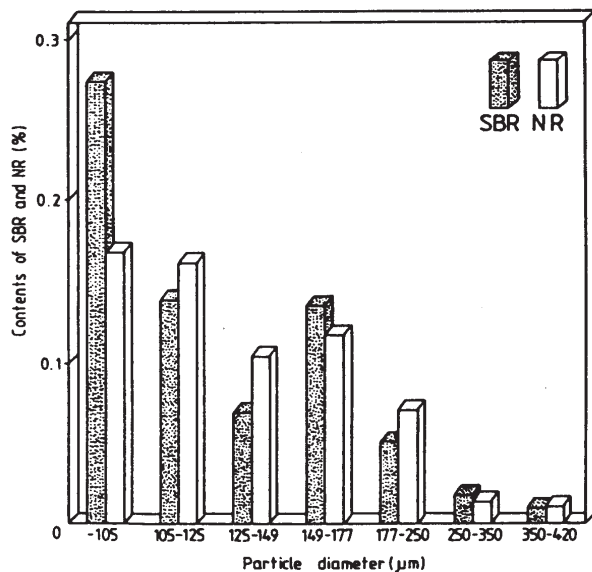


Fig. 7. Distribution of contents of SBR and NR tire tread rubbers in piled particulate matter at the entrance to a tunnel on the highway.

rubber collected at the entrance of the tunnel was highest. This was probably attributable to the fact that the highway is curved substantially at a right angle near the entrance, and some of the cars running along the highway brake at that point, which results in an increase in the amount of abrasion of the tire tread rubbers. The contents of SBR and NR tire tread rubbers at a distance of 20 m from the entrance of the tunnel were very low; viz. 0.0201 and 0.0116 wt.%, respectively.

Fig. 7 shows the size distribution of the SBR and NR tire tread rubber particles contained in piled particulate matter collected at the entrance of the tunnel. As the particle size decreased, the contents of the SBR and NR tire tread rubber particles increased. Accordingly, from the environmental viewpoint, it is important to monitor the movement of small rubber particles or dusts with a particle size below about 100 μ m, which are readily scattered by wind and the like.

The determination limits (signal-to-noise ratio) of this method for SBR and NR tire tread rubbers in piled particulate matters were 12.2 and 38.6 μ g based on 1 g of the piled particulate matter, respectively. The relative standard deviations of the measured contents of the SBR and NR tire tread rubbers were less than 10%.

This method is effective in approximately determining the content of SBR and NR tire tread rubbers in piled particulate matter on highway both simply and quickly.

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