

Mechanical Aging Behavior of Styrene-Butadiene Rubbers Evaluated by Abrasion Test

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ABSTRACT: The ring-shaped styrene-butadiene rubbers (SBRs) test pieces ran on a rotating stainless-steel ring using an abrasion tester to evaluate the changes in the mechanical properties, such as the tensile storage modulus and $\tan \delta$ values, the modulus at 300% elongation, and the strength and extension ratio at the breaking point, after a mechanical aging process. The surface of the SBR test pieces and the formed rubber debris after the running experiment was investigated using scanning electron microscopy. A change in the crosslinking density of the SBRs

and the analysis of the isolated free polymers showed the occurrence of bond scission of the copolymer chains. On the other hand, the mechanical properties of whole SBR samples showed only a small change during the mechanical aging test. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 379–389, 2011

Key words: abrasion test; free polymer; mechanical aging; mechanical properties; polymer degradation; styrene-butadiene rubber; rubber debris

INTRODUCTION

The mechanical properties of rubber materials are significantly influenced by thermal and mechanical degradation during their use over a long period.^{1–7} Therefore, high-performance rubber materials have been developed for use with diverse purposes that demand excellent physical and mechanical properties and long-term stability.^{8–16} Styrene-butadiene rubbers (SBRs) are used for the tire tread, which is the most important component for total tire performance for automobiles.^{17–23} It is actually accepted on the basis of numerous practical data that the properties of materials used for the tire tread show a great change after running for a long distance and time. However, there are few clear experimental data and rational explanation for elucidating the mechanism of the deterioration of the materials during running.

Recently, we investigated the changes in the mechanical properties of SBRs with different styrene, 1,2-, and 1,4-butadiene contents and molecular weights before and after a thermal aging process to evaluate the effect of the polymer structures on the thermal aging of the SBR vulcanizates.²⁴ As a result, we observed the fact that hardness and modulus values increased during the degradation of the poly-

mer chains, but the change was smaller than that we expected. Furthermore, we and Kataoka et al.²⁵ revealed a significant effect of the evaporation of oily components, which were added as a plasticizer for the vulcanization process. On the other hand, constant mechanical properties were observed during thermal aging when liquid polymers were used as the nonvolatile plasticizers.²⁶ These experimental results indicate that the used SBRs are thermally stable and retain constant physical properties under heating conditions for a long time. Therefore, we started to examine the mechanical aging of the SBRs. There are a large number of studies on the abrasion and wear of rubber materials in the literature.^{23,27–35} Several types of mechanisms are proposed for the wear of metals, glasses, rubbers, and other materials. For example, abrasive wear, adhesive wear, surface fatigue, and corrosion occur depending on many factors, such as the nature of the materials and surfaces, additives, temperature, and strain. Among them, abrasive wear mechanism is the most important for the wear of rubber materials. In general, however, it is difficult to precisely reproduce mechanical aging data using actual tires, because the conditions used for the endurance testing of tires are not simple and many factors should be considered for understanding the change in the tire performance during long-time use. In this study, we used a simple apparatus for evaluating the mechanical aging process of the SBRs. The SBRs were prepared without additives and carbon blacks to more precisely evaluate the effect of the mechanical aging on

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TABLE I
Formulation of SBR vulcanizates^a

Materials	Relative weight
SBR	100
Process oil ^b	25
Stearic acid	1.25
Zinc oxide	2.50
Accelerator (TBBS) ^c	1.25
Sulfur	1.25

^a Vulcanization was carried out at 170°C for 20 min.

^b Process X-260 (Japan Energy Co.).

^c TBBS: *tert*-butyl benzothiazole-2-sulfenamide.

the mechanical properties of the SBR vulcanizates.²⁴ We adopted a rotating-type abrasion test using a laboratory abrasion tester to investigate changes in the structures and the mechanical properties of the SBRs during the mechanical aging process.

EXPERIMENTAL

Materials

We used three kinds of SBR samples with different styrene, 1,2-, and 1,4-butadiene contents, which were synthesized on a laboratory scale in our previous study.²⁴ The samples included no antioxidants and stabilizers. The SBR compounds, which were made of SBR, process oils, stearic acid, zinc oxide, an accelerator, and sulfur, were mixed, fabricated in the shape of a sheet, and cured at 170°C for 20 min. The conditions are summarized in Table I. We used no further additives and carbon blacks to more precisely evaluate the effect of the mechanical aging on the mechanical properties of the SBR vulcanizates. Commercial solvents were used as received without further purification for the extraction experiments. The polymer chain structure, molecular weight and its distribution, and T_g values are presented in Table II.

General measurements

The weight-average molecular weight (M_w) and polydispersity (M_w/M_n) were determined by gel permeation chromatography (GPC) using a Shimadzu

RID-6A equipped with a refractive index (RI) as the detector and standard polystyrenes for calibration. The structure of the SBR was determined by nuclear magnetic resonance spectroscopy using a Bruker Advance II 400 spectrometer and chloroform-*d* as the solvent at room temperature. The glass transition temperature (T_g) was determined by differential scanning calorimetry (DSC) using a Seiko DSC-6200 at the heating rate of 10°C/min. Scanning electron microscopic (SEM) observation was carried out using Horiba XL30-ESEM (5 kV) in low (300×) and high (1000×) magnifications.

Abrasion test

The ring-shaped test pieces of the SBRs were prepared for an abrasion test. The diameter (D), width (W), and thickness (T) of the test pieces were 76, 17, and 21 mm, respectively. The abrasion test was carried out using a laboratory abrasion tester (VMI Holland BV, LAT100). A constant load (50 N) was applied to the ring-shaped test piece, which ran on a stainless-steel ring rotating at a speed of 30 km/h. The test piece was set at an angle (θ) from the running direction. Samples A–C were fixed at an angle θ of 0, 5, and 10° and were allowed to run for a distance of 40 and 80 km on the stainless-steel ring maintained at 10, 50, and 80°C, as shown in Figure 1. In this study, stainless steel was used instead of whetstone, which is often used for the typical abrasion test of tires. This is because the SBR vulcanizates, which included no additives and carbon blacks, were too rapidly worn during the running on whetstone. After the test at a given temperature and time, that is, a distance for the running, the surface of the test pieces was removed out at ~0.5-mm average thickness to obtain test pieces with a flat surface. The samples were then sliced to obtain sheets with a 1-mm thickness for the preparation of the test pieces used for each measurement to determine the mechanical properties.

Mechanical properties

The viscoelasticity measurement was carried out using an Iwamoto VES-F-III viscoelastic analyzer at

TABLE II
Characterization of styrene-butadiene copolymers used in this study

Sample code	Polymer chain structure (%) (NMR)			$M_w \times 10^{-6}$ (GPC)	M_w/M_n (GPC)	T_g^a (°C) (DSC)
	Styrene	1,2-Butadiene	1,4-Butadiene			
A	40.8	30.0	29.2	1.33	1.18	−27.8
B	30.4	33.0	36.6	1.57	1.24	−37.2
C	39.9	12.0	48.1	1.17	1.21	−52.0

^a After vulcanization.

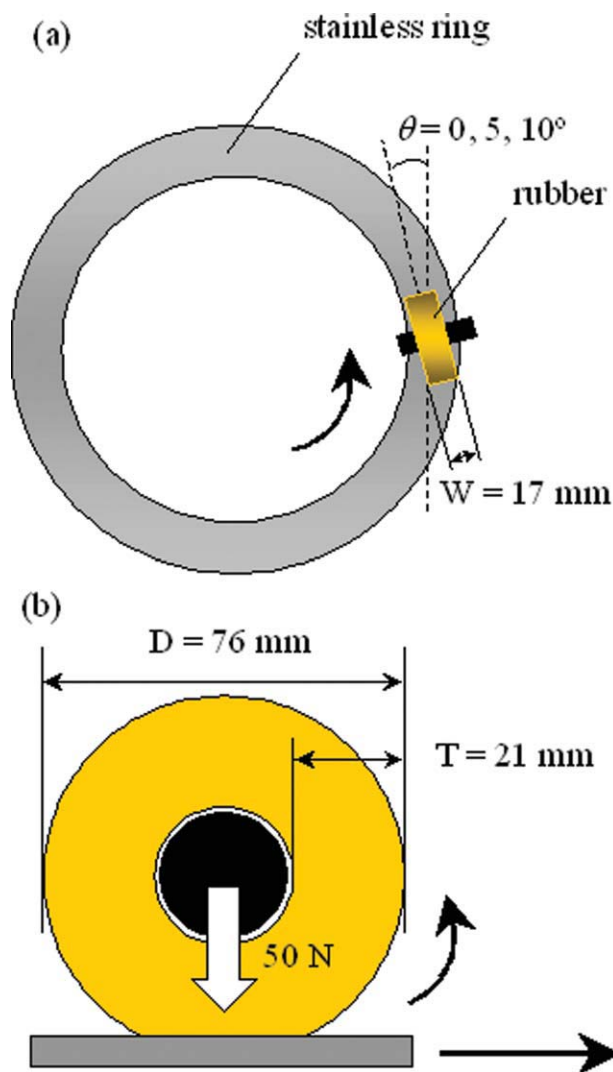


Figure 1 Illustrative representation of the ring-shaped SBR test piece (a) fixed at the angle θ and (b) with an applied constant load (50 N) on a rotating stainless-steel ring. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

a 12% distortion, a frequency of 10 Hz, and 25°C, according to JIS K6394 (ISO 4664-1: 2005), to determine the tensile storage modulus (E^*) and $\tan \delta$ values. The measurements were carried out using five test pieces with a 1-mm thickness, and an average value and standard deviation were determined. The tensile experiment was carried out using a Shimadzu AGS-500 apparatus, according to JIS K6251 (ISO 37: 1994, ASTM D624). A dumbbell-shaped sample (35 mm \times 6 mm) with a 1-mm thickness was loaded in tension at the rate of 200 mm/min, and the modulus was recorded at 300% elongation (M_{300}). The strength (σ_b) and the extension ratio (λ_b) at the tensile breaking point were also determined. The sample number for the tensile test was three, and the median was recorded as the data.

Cyclic tensile test

A cyclic tensile test was carried out using a Shimadzu AGS-500 apparatus. The test pieces were of a dumbbell shape (100 mm \times 25 mm) and 2-mm thickness. The rate was kept at 200 mm/min. The maximum stress was 1.0 or 1.2 MPa, and the cycle was repeated 10 and 100 times. The measurements were carried out using six test pieces, and an average value and standard deviation were determined. After the cyclic tensile test, the viscoelasticity measurement, the swelling test, and the solvent extraction were carried out.

Crosslinking density

The crosslinking density, ν (mol/mL) was calculated by the Flory-Rehner equation [eq. (1)].³⁶

$$\nu(\text{mol/mL}) = \frac{v_R + \ln(1 - v_R) + \chi v_R^2}{-V_0(v_R^{1/3} - v_R/2)} \quad (1)$$

where v_R is the volume fraction of the polymer after swelling, which was determined by the volumes of the polymers before and after being immersed in toluene at 25°C for 24 h, according to JIS K6258 (ISO 1817: 1999) [eq. (2)]. Typically, 0.2 g of the polymer and 15–20 mL of the solvent were used for the swelling test. V_0 and χ are the molecular volume of the solvent and the interaction parameter, respectively. In this study, we used the following values: $V_0 = 106.7$ mL, $\chi = 0.352\text{--}0.365$.

$$v_R = \frac{\text{Volume of dry polymer}}{\text{Volume of swelled polymer}} \quad (2)$$

Solvent extraction

To isolate the soluble fractions of the SBR samples, successive extractions were carried out using acetone and chloroform under reflux conditions. First, the acetone extraction (AE) value was determined as the weight fraction of the acetone-soluble part by extraction with acetone under reflux for 24 h. Subsequently, the chloroform extraction (CE) value was determined by reflux with chloroform for 24 h using the same sample after the AE. Each extraction procedure was carried out using 0.2 g of the polymer and 150–200 mL of the solvent. The extracts were isolated as the AE and CE fractions after evaporating the solvents. After the extraction with chloroform, the residue was further extracted using tetrahydrofuran (THF), and the obtained extract was then analyzed by GPC measurement to determine the M_w values.

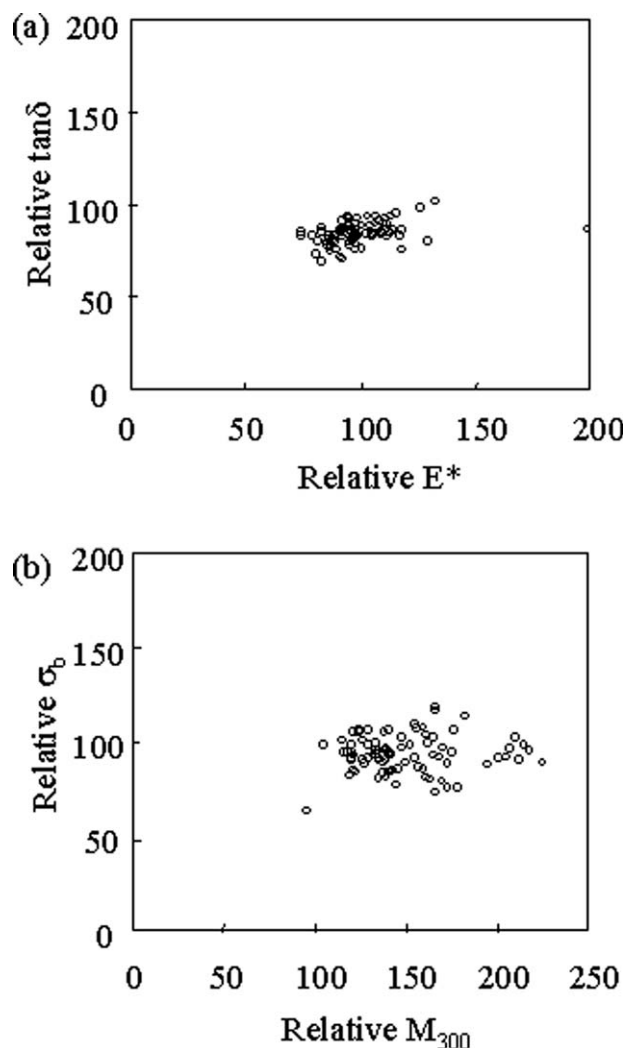


Figure 2 Change in (a) the relative E^* and $\tan \delta$ values and (b) the relative M_{300} and σ_b values for the tire tread after running on a road at 100–150 km/h for ~ 1 h.

RESULTS AND DISCUSSION

Change in tire property during running

The mechanical properties of the rubbers used for the tire tread showed a great change after actual running on a road. Figure 2 shows the results for the evaluation of the mechanical properties of the tire treads after running at a speed of 100–150 km/h for ~ 1 h. The data were collected for several runs under various conditions. The E^* and $\tan \delta$ values were determined by viscoelastic measurement and the M_{300} , σ_b , and λ_b values by tensile measurement. Each value after running is shown as the relative value versus the value determined for a new tire before running. The change in the E^* and $\tan \delta$ values was relatively small. The $\tan \delta$ value decreased by 0–25%, whereas the data for the E^* value were scattered in a range of 70–130%. For the data for the tensile experiments, the M_{300} value largely increased

to 110–230%, and a change in the σ_b value was random in the range of the 70–120%. In general, the decreasing $\tan \delta$ and the increasing M_{300} values are often observed during actual running tests using tires. The data shown in Figure 2 agree well with this general tendency.

In our preliminary study on the thermal aging behavior,²⁴ we revealed an increase in the modulus and $\tan \delta$ values of the SBRs during heating for a long period over several weeks. We further pointed out the significant effect of the slow evaporation of the process oils used as the plasticizers. Actually, constant mechanical properties were confirmed using the nonvolatile liquid polymers as the plasticizers.²⁶ The results shown in Figure 2 cannot be explained only by the thermal aging effects, and this suggests that other factors, such as mechanical aging, are important for the deterioration of the rubber materials. Therefore, we tried to evaluate the mechanical aging effect of the SBRs using a model experiment in a laboratory.

Abrasion test and SEM observation

In this study, we used a modified rotating-type abrasion test, but not a conventional DIN-type abrasion test, because we need an experiment close to the actual running conditions for tires.

The test pieces were worn during the abrasion test, and a considerable amount of rubber debris was formed under the conditions at a high temperature and a large θ value. An abrasion pattern was observed on the surface of some samples and smoothness depended on the conditions for the abrasion test. In general, sets of parallel ridges, called abrasion patterns, are found on the surface of the rubber samples when they are abraded in one direction.²⁸ As shown in the SEM images in Figure 3, no abrasion pattern was observed on the surface of Sample C after running at 5° of the θ value, independent of the temperature. The roughness of the sample surfaces increased when the temperature increased to 50 or 80°C . On the other hand, a typical abrasion pattern was formed under the running conditions at 10° of the θ value [Fig. 3(d)]. This is because the increment of the θ value causes greater friction at the rubber surface.²⁸ The amount of the formed rubber debris depends on the increase in the surface roughness and the abrasion pattern generated when the rubber is largely deformed by the stress. Similar abrasion patterns were also observed for the other samples, A and B, under similar running conditions at 10° of the θ value (Fig. 4), irrespective of the repeating structure of the styrene-butadiene copolymers.

The debris formation and the generation of abrasion pattern are accounted for by the temperature

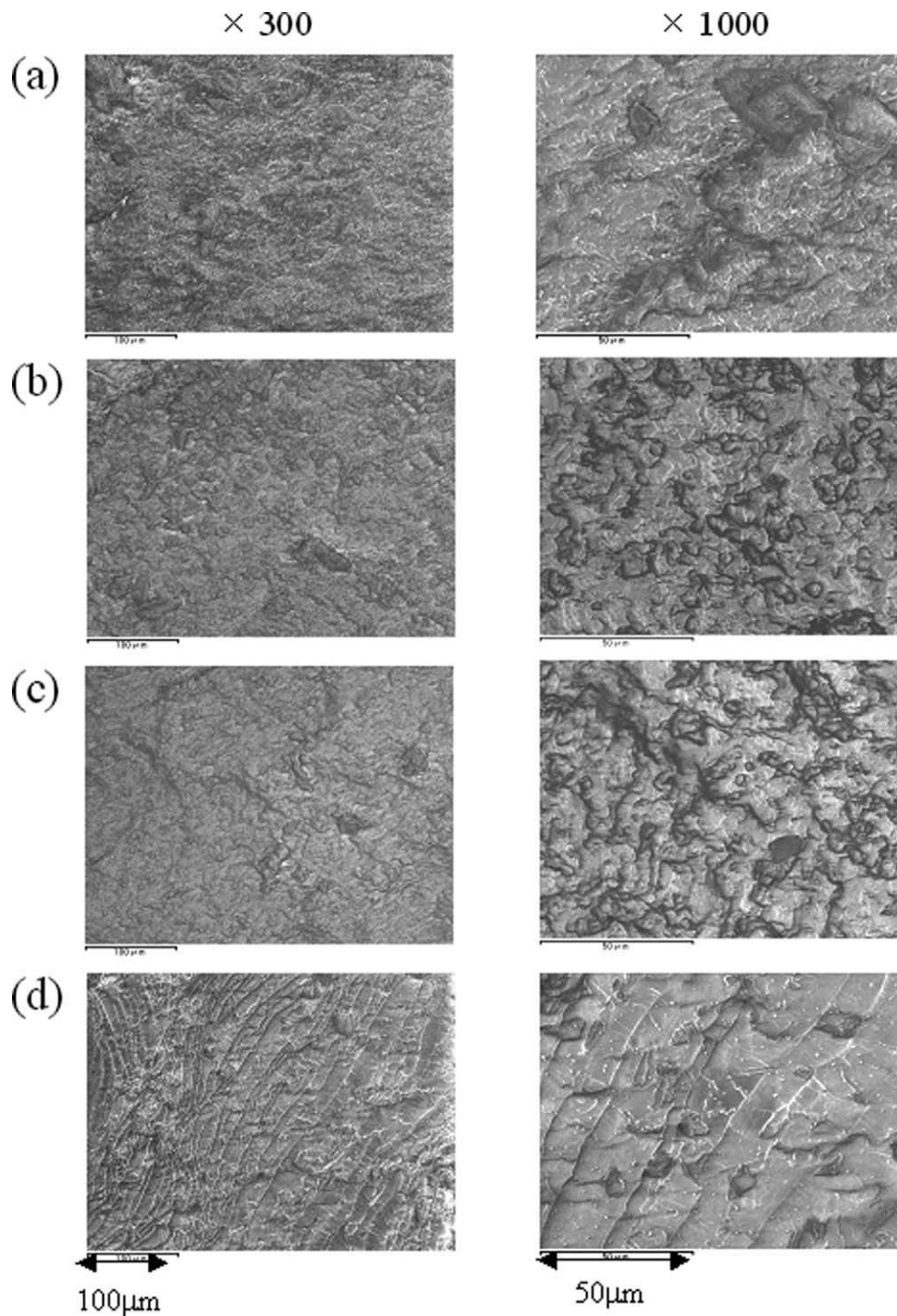


Figure 3 SEM images in low ($\times 300$) and high ($\times 1000$) magnifications for the surface of Sample C after 10-km running at 5° of the θ value and (a) 10°C, (b) 50°C, and (c) 80°C, and (d) after 3.3-km running at 10° of the θ value and 50°C.

dependence of the sample modulus. Figure 5 shows the E^* values for Samples A–C as the function of the temperature. All the samples have similar E^* values (1.05–1.14 MPa) at 50°C. In short, the samples can be deformed in a similar fashion in a temperature region over 50°C, whereas the E^* value of each sample at a lower temperature significantly depends on the structure of the polymers; E^* values at 10°C were 11.9, 1.36, and 2.66 MPa for Samples A, B, and

C, respectively. The amount of the formation of the rubber debris was dependent on the kind of the polymers.

In the literature, oily debris was usually formed during an abrasion test using SBR in the air.^{32,37,38} In this study, dry debris was formed independent of the temperature, as shown in Figure 6. Chemical reactions readily occur at the sample surface during a conventional abrasion test, because a blade is

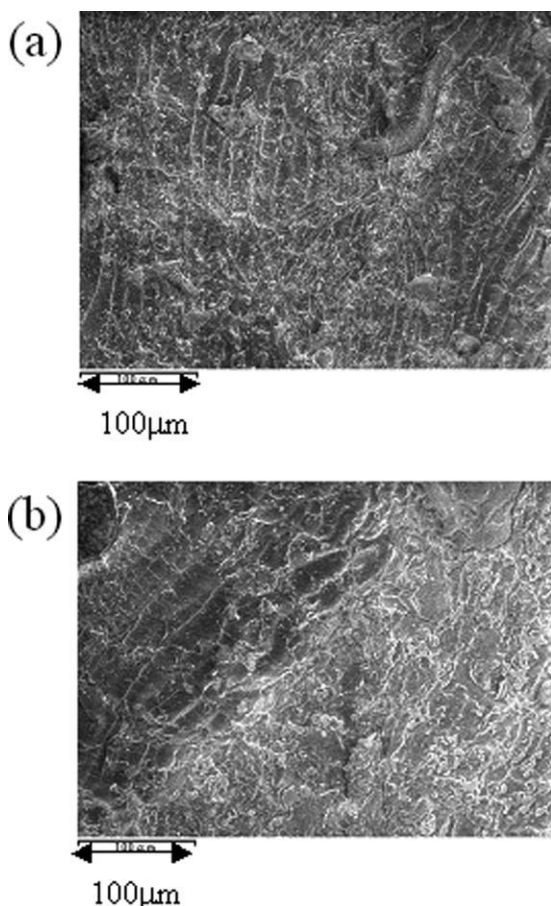


Figure 4 SEM images for the surface of (a) Sample A and (b) Sample B after 3.3-km running at 10° of the θ value at 50°C ($\times 300$).

slidden on the nonrotating sample implying carbon blacks and a locally generated frictional heat rises the temperature of a sample surface. A decrease in the molecular weight of the polymers results in an oily debris formation. To check an increase in the temperature, we measured the temperature of the rubber surface during the running experiments using a radiation thermometer. Figure 7 shows a change in the temperature of the rubber surface when the road surface (a rotating stainless steel) was maintained at 80°C .

The temperature of the sample surface of B and C increased from room temperature and achieved to a constant value at 76°C after 4-km running, whereas the temperature of Sample A gradually increased to 80°C after 20 km. The difference is related to the wearing of samples. The weight loss of Sample A is only 4% after running, and a friction heat gradually rises the sample temperature of A. On the other hand, debris is easily formed for the cases of Sample B and Sample C and consequently a fresh surface appear during the test (The weight loss of sample reach 24–25%). For all three experiments, the temperature of the sample surface did not exceed 80°C .

In conclusion, there is no effect of the overheating by a friction heat, and no occurrence of significant chemical reactions inducing a decrease in the molecular weight of polymers. The sample used in this study contains no carbon black and has a low-tan δ value. A difference in the methods of an abrasion test is also one of the reasons why the dry debris is formed in this experiment. The apparatus for our abrasion test implies a rotating sample system, in which less friction is generated during the test.

Mechanical properties

The viscoelastic and tensile mechanical properties were evaluated for the samples after the running under various conditions. The obtained E^* , $\tan \delta$, M_{300} , σ_b , and λ_b values are presented in Table III. We also evaluated the crosslinking density based on the swelling data for the samples.

It was previously demonstrated that the E^* and M_{300} values increased because of an increase in the crosslinking points and the evaporation of oily components during thermal aging, irrespective of the repeating structure of the styrene-butadiene copolymers.^{24,26} In contrast, it was revealed that only a small change was observed during the mechanical aging test in this study, as shown in the experimental values for the mechanical properties and the crosslinking density in Table III. The E^* – $\tan \delta$ and M_{300} – σ_b relationships after the mechanical aging test are plotted in Figure 8. No dependence on the polymer repeating structures was observed in both relationships. When these results were compared with those for the running test using actual tires in Figure 2, some of the $\tan \delta$ values increased after

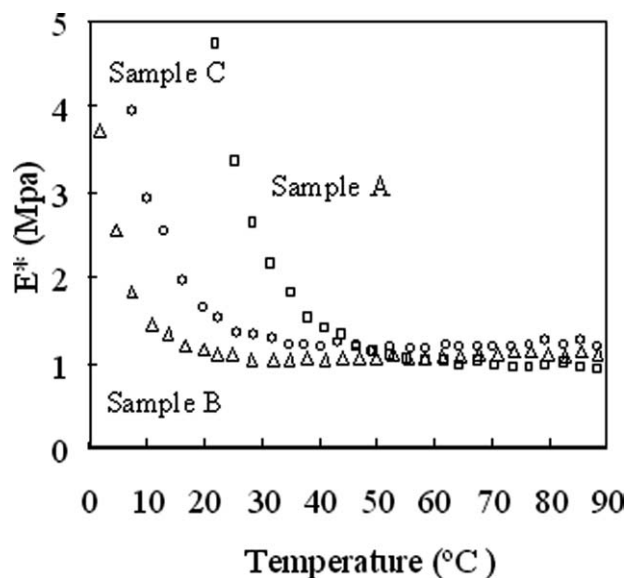


Figure 5 Temperature dependences of tensile storage modulus (E^*) for Samples A–C.

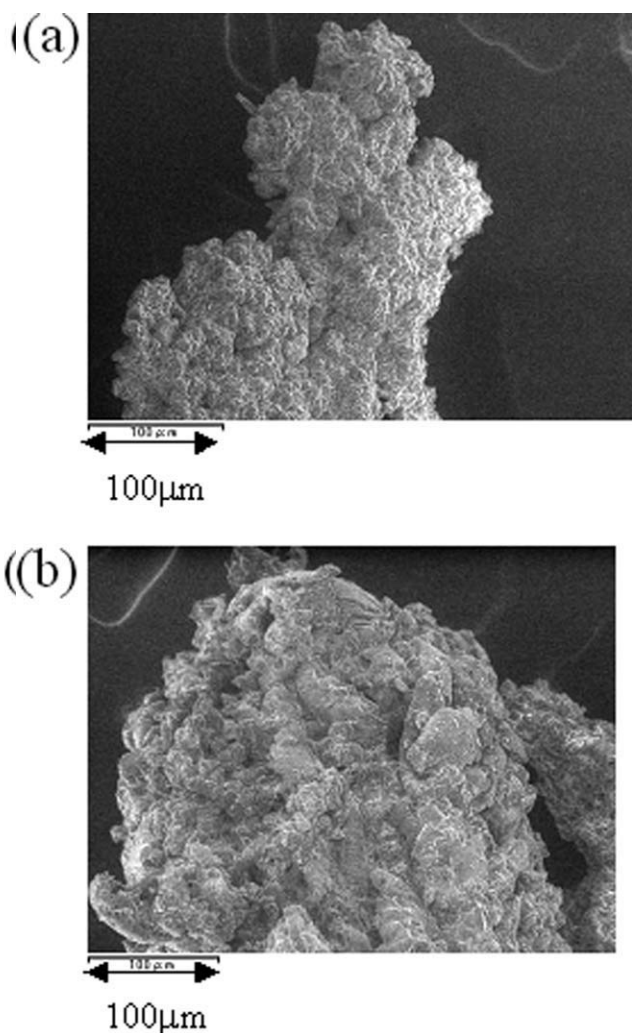


Figure 6 SEM images for the surface of debris produced from Sample C during running at 5° of the θ value at (a) 10°C and (b) 80°C ($\times 300$).

running in Figure 8, whereas all the $\tan \delta$ values decreased in Figure 2. The distribution of the plots for the E^* and $\tan \delta$ values was narrower in the case of Figure 8. An increment in the M_{300} values showed similar tendency. Some of the σ_b values increased and others decreased during the mechanical aging process in both cases of Figures 2 and 8. The σ_b values include a large experimental error, because the breaking of the sample is a macroscopic event for the materials, and the breaking point is determined by the characteristics of the weakest area in the samples. It is difficult to strictly discuss the changes in the σ_b value for the aging of a tire used under actual running conditions.

Structure of polymers

The formed rubber debris was collected and analyzed by solvent-extraction experiments and GPC measurement. Table IV summarizes the results for

the characterization of the soluble fractions isolated from the SBR samples of both the rubber surface and the rubber debris. After the oily and low-molecular-weight components were first extracted with acetone (AE fraction), the soluble and free polymers with a relatively low-molecular-weight were extracted from the residue using chloroform (CE fraction). Furthermore, high-molecular-weight polymers were extracted using THF and their M_w values determined by the GPC measurement.

The formation of the rubber debris was dependent on the kind of the polymers and the running conditions, such as the temperature and the angle θ . The debris was readily formed for Samples B and C at 50 and 80°C at 5 and 10° of the θ value, whereas no

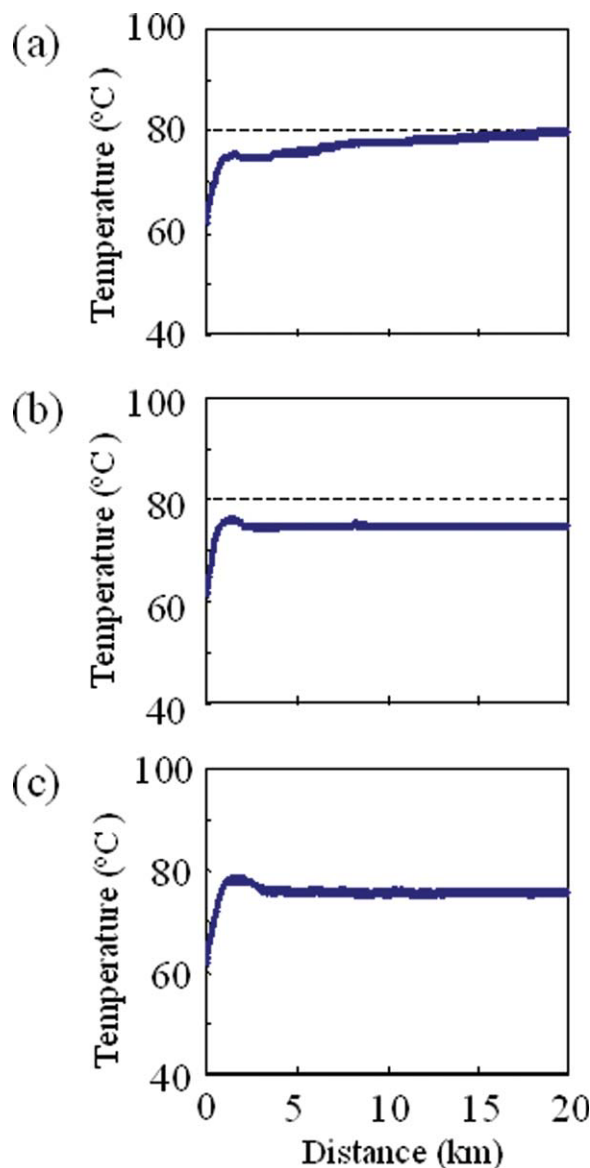


Figure 7 Change in the temperature of the sample surface during running: (a) Sample A, (b) Sample B, and (c) Sample C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
Mechanical and swelling properties of the SBRs after mechanical aging test under various conditions

Sample code	Running condition			Viscoelasticity		Tensile test			Swelling test	
	Distance (km)	Temperature (°C)	θ (°)	E^* (MPa)	Tan δ	M_{300} (MPa)	σ_b (MPa)	λ_b (%)	Swelling (%)	$v \times 10^4$ (mol/mL)
A	0	–	–	2.05 ± 0.16	0.450 ± 0.022	1.66	5.40	593	487	1.28
	40	10	5	1.94	0.453	1.80	4.94	574	487	1.28
	40	50	5	1.83	0.434	1.72	6.02	609	497	1.23
	40	80	0	1.98	0.440	2.03	5.95	512	488	1.27
	40	80	5	1.64	0.383	1.72	4.61	572	494	1.24
	40	80	10	2.00	0.434	2.06	6.01	507	482	1.31
	80	50	5	1.78	0.396	1.77	6.13	602	493	1.25
B	0	–	–	1.10 ± 0.05	0.126 ± 0.005	1.49	3.59	514	475	1.35
	40	10	5	1.03	0.137	1.62	3.60	546	471	1.38
	40	50	5	1.01	0.128	1.51	4.29	581	505	1.19
	40	80	0	1.11	0.122	1.79	2.48	507	477	1.34
	40	80	5	1.11	0.119	1.55	3.99	529	464	1.43
	40	80	10	1.12	0.117	1.39	2.80	512	669	0.67
	80	50	5	1.10	0.135	1.62	4.64	589	484	1.31
C	0	–	–	1.43 ± 0.06	0.182 ± 0.010	1.55	3.60	537	439	1.59
	40	10	5	1.40	0.194	1.72	4.31	596	449	1.52
	40	50	5	1.39	0.191	1.71	4.48	594	444	1.56
	40	80	0	1.44	0.185	1.39	2.80	512	434	1.63
	40	80	5	1.45	0.177	1.53	5.57	674	443	1.56
	40	80	10	1.50	0.171	1.81	5.69	625	428	1.68
	80	50	5	1.41	0.192	1.74	5.01	616	446	1.54

formation of debris was observed under the conditions at the temperature of 10°C and with an angle θ of 0°. For Sample A, a small amount of debris was formed only under limited conditions. The amount of the formed debris was determined to be 4, 25, and 24% for Samples A, B, and C during the running at 80°C with a θ of 10°. These conditions provided the largest amount of debris for each sample. The amount of the AE fraction (i.e., the amount of the oily and low-molecular-weight components) was constant as 20.5–23.0% and 21.0–23.7% for the rubber surface and the debris, respectively. On the other

hand, the amount of the CE fraction for the rubber debris was high (0.6–5.8%) compared with the low values for the rubber surface (0–0.6%). This indicates that a large amount of the chloroform-soluble and low-molecular-weight polymers are included in the debris. For the rubber surface, THF-soluble and high-molecular-weight polymers were not detected by GPC analysis, except for the case performed with Sample B at 80°C and a θ of 10°. In this case, the free polymers with an M_w of 9.3×10^4 were included. The swelling test of Sample B after running at 80°C and a θ of 10° also provided results

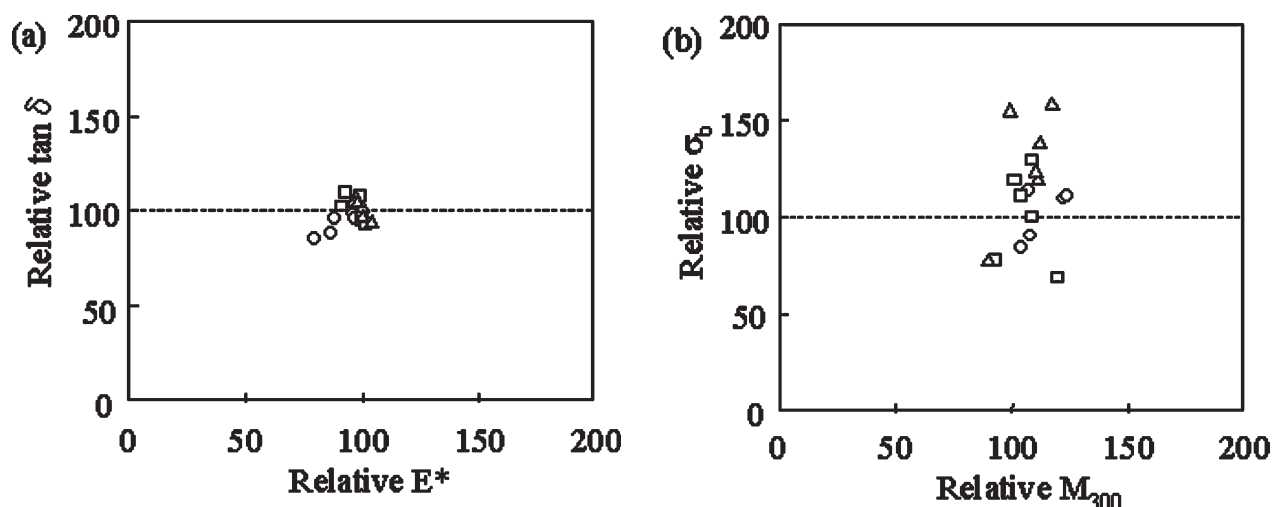


Figure 8 Change in (a) the relative E^* and tan δ values and (b) the relative M_{300} and σ_b values for the SBRs after running using a laboratory abrasion tester under various conditions, presented in TABLE II. (○) Sample A, (□) Sample B, and (△) Sample C.

TABLE IV
Characterization of the soluble fractions of the SBRS after mechanical aging test

Sample code	Running conditions			Rubber surface			Rubber debris			
	Distance (km)	Temperature (°C)	θ (°)	AE (%)	CE (%)	$M_w \times 10^{-4}$ (GPC)	Formation (yield ^a %)	AE (%)	CE (%)	$M_w \times 10^{-4}$ (GPC)
A	0	–	–	21.8	0.2	–	No	–	–	–
	40	10	5	22.1	0.1	–	No	–	–	–
	40	50	5	22.1	0.1	–	No	–	–	–
	40	80	0	22.3	0	–	No	–	–	–
	40	80	5	22.3	0.1	–	Yes (–) ^b	23.5	2.0	–
	40	80	10	22.5	0	–	Yes (4)	23.1	2.1	5.3
	80	50	5	22.1	0	–	No	–	–	–
B	0	–	–	21.1	0.1	–	No	–	–	–
	40	10	5	20.5	0.1	–	No	–	–	–
	40	50	5	20.8	0	–	Yes (–) ^b	22.9	2.2	1.7
	40	80	0	20.8	0	–	No	–	–	–
	40	80	5	20.6	0.1	–	Yes (–) ^b	21.4	2.1	2.8
	40	80	10	21.4	0.5	9.3	Yes (25)	21.0	1.0	6.6
	80	50	5	20.7	0	–	Yes (–) ^b	23.7	5.8	2.3
C	0	–	–	21.5	0.2	–	No	–	–	–
	40	10	5	22.4	0	–	No	–	–	–
	40	50	5	22.1	0.1	–	Yes (–) ^b	23.6	2.1	–
	40	80	0	22.2	0.1	–	No	–	–	–
	40	80	5	22.1	0.2	–	Yes (–) ^b	23.5	1.9	–
	40	80	10	23.0	0.6	–	Yes (24)	22.7	0.6	5.0
	80	50	5	22.2	0	–	Yes (–) ^b	23.7	2.4	–

^a Determined based on the weight loss of the test pieces of the SBRS.

^b Not determined.

different from all the other cases; the degree of swelling was 669%, and the crosslinking density, ν , was 0.67×10^{-4} mol/mL, as shown in Table III and Figure 9. Differing from the specific feature of the swelling test, the mechanical properties evaluated by the viscoelastic and tensile measurements are similar to the others (Table III).

The increment in the CE fraction and the detection of the THF-soluble polymers in the rubber debris indicate the formation of the free polymers by the more frequent occurrence of the polymer chain scission in the SBR networks. The bond scission occurs when the stress is repeatedly applied to the sample, and the strain is concentrated at specific positions in the crosslinked networks of the polymers. Because Samples B and C are composed of more flexible polymers with a low T_g (–37.2 and –52.0°C, respectively), larger deformation is possibly induced during the running test under the conditions with the same magnitude of the entire applied stress. The M_w values of the free polymers obtained from the rubber debris were dependent on the temperature and the angle. The M_w values were 5.0 – 6.6×10^4 under the conditions at which the largest amount of debris was formed, i.e., at 80°C and a θ of 10°. At a lower temperature or with a lower θ angle, the M_w decreased to 1.7 – 2.8×10^4 . These M_w values of the polymers isolated from the debris were smaller than that of the rubber surface (9.3×10^4). After all, when

a larger strain was applied to the samples, the M_w value of the free polymers in the debris increased.

Cyclic tensile test

We investigated the conditions for the bond scission and the formation of free polymers using the cyclic

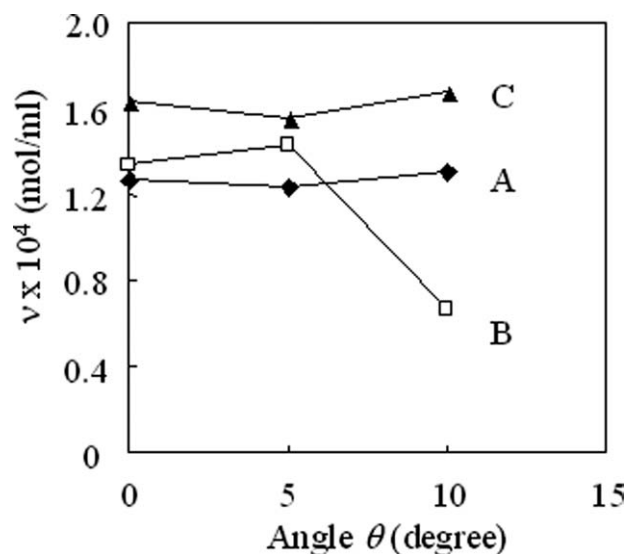


Figure 9 Change in the crosslinking density (ν) of the SBRS during the mechanical aging test.

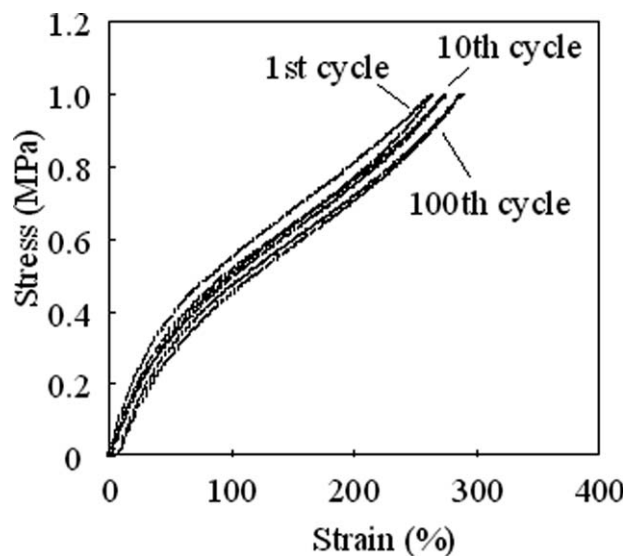


Figure 10 The results of a cyclic tensile test for Sample B. The maximum stress was at 1.0 MPa, and the cycle number was 1, 10, and 100.

tensile test. The σ_b value was determined to be 1.56 ± 0.35 MPa for Sample B, which is lower than that for the σ_b value of Sample B used in the abrasion test ($\sigma_b = 3.59$ MPa, shown in Table III). When two test pieces of Sample B were provided for the cyclic tensile test at the maximum stress value of 1.2 MPa, the test pieces were broken after three and 10 cycles. We checked the CE fraction of the broken samples, similar to the experiment described earlier. The other samples were cut from the broken test pieces near the broken point, and the amount of the free polymers was determined. As a result, we detected no free polymer in the broken samples. This suggests that the whole polymer network structure suffered no serious damage when the applied force reached a sufficient value to cause a breakdown.

The test pieces of Samples A–C were provided for the cyclic tensile test at the maximum stress of 1.0 MPa with a cycle number of 10 and 100. All the

measurements were successfully carried out without breakage of the samples. The stress-strain curves obtained during the cyclic tensile test are shown in Figure 10. The increase in the elongation was small, and the shape of the curves appeared irrespective of the cycle number. After the cyclic tensile test, the test pieces were further cut at the center of the piece to obtain a test piece with a 10-mm length for the viscoelastic measurement and the swelling test. The E^* and $\tan \delta$ values and the degree of swelling determined are presented in Table V. All the mechanical properties and the swelling data showed constant values and a small CE fraction (0–0.1%), independent of the cycle numbers. This result indicates that the crosslinking points in the SBRs are not broken and that free polymers are not formed by an applied stress close to the σ_b value and after 100 cycles.

Mechanical aging effect

In this study, we have revealed that no free polymers are included in both the samples of the rubber surface and debris under the conditions at an angle of 0° and at 80°C . On the other hand, a considerable amount of the free polymers were detected under the conditions with larger angles, such as 5° and 10° . The free polymer formation is considered to be due to the mechanical aging effect but not thermochemical effect. Based on the results of the abrasion tests, the bond scission of the polymer chains in the SBR networks occurs, and it generates the free polymers when the stress is repeatedly applied to the sample. The frequently occurring chain scission finally results in the formation of rubber debris. On the other hand, no free polymer was included in the rubber surface, although the applied force may induce a large deformation of the whole rubber. This can be explained by the applied stress focused at a local area in the sample. An extraordinary large number for the repeatedly applied force is also

TABLE V
Properties of the SBRs after cyclic tensile test

Sample code	Cycles	Viscoelasticity		Swelling test		Extraction	
		E^* (MPa)	Tan δ	Swelling (%)	$v \times 10^4$ (mol/mL)	AE (%)	CE (%)
A	0	2.11 ± 0.07	0.471 ± 0.035	485	1.20	21.7	0.1
	10	2.20	0.474	485	1.20	— ^a	— ^a
	100	2.21	0.495	490	1.16	22.1	0.1
B	0	1.11 ± 0.03	0.145 ± 0.015	476	1.31	20.0	0.1
	10	1.14	0.142	476	1.31	— ^a	— ^a
	100	1.13	0.127	440	1.54	20.5	0
C	0	1.46 ± 0.03	0.207 ± 0.015	445	1.51	21.3	0.1
	10	1.52	0.200	445	1.51	— ^a	— ^a
	100	1.42	0.191	430	1.62	21.9	0.1

^a Not determined.

important for the polymer damage during the running experiments using a ring-shaped and rotating SBR test pieces. The times of the applied force, that is, the number of the rotations of the test sample during the abrasion test, are more than 10^5 , which is 10^3 times larger than the cycle number for the cyclic tensile test in this study. Therefore, no significant chain scission occurred even under the conditions near the breaking point for the tensile experiment in Table V.

As a result of the thermal aging, the process oil slowly evaporated during the heating, and it changed the mechanical properties of the SBR.^{24–26} Furthermore, constant mechanical properties were observed during the thermal aging when the liquid polymers were used as nonvolatile plasticizers for the vulcanization process.²⁶ On the basis of the results for the changes in the mechanical properties during the mechanical aging, we conclude that the crosslinking points in the SBRS are hardly broken unless an extremely large force is applied and that the SBR vulcanizates are stable to both the thermal and mechanical aging processes.

CONCLUSIONS

Based on the change in the structure and mechanical properties of the SBRS during a mechanical aging test using a laboratory abrasion tester, it was revealed that the SBRS show a small change in the mechanical properties and that the crosslinking points are hardly broken by mechanical force, except for the case under the conditions including an extremely large stress. In general, a change in the mechanical properties of the tire tread compounds after running is accounted for by an increase in the crosslinking points due to the thermal and mechanical deterioration of the materials. In our present and previous studies, however, we have revealed that the SBR vulcanizates are essentially stable against thermal and mechanical aging based on the results obtained from the model experiments under the proper conditions. These results suggest that any other factor, such as an interaction between the polymers and the added carbon blacks, should be additionally considered to fully explain the change in the mechanical properties after running of the automobile tires. We are now continuing further investigation to design a new tire including less change in the mechanical properties during use.

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