# Change in Mechanical Properties of Styrene-Butadiene Rubber Vulcanizates during Thermal Aging

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## Synopsis

The change in mechanical properties was investigated during the thermal aging process of styrene-butadiene rubbers (SBR) with different styrene, 1,2-, and 1,4-butadiene contents and the different types of plasticizers. An increase in the hardness and modulus values during the aging was confirmed to be due to the additional cross-linking reaction between the polymer chains in the SBR vulcanizates and the slow evaporation of the used process oil. We demonstrated the validity of the use of a nonvolatile liquid polymer as the plasticizer to achieve the desired physical properties of the SBR vulcanizate during thermal aging.

**KEYWORDS:** Cross-Linking, Liquid Polymer, Mechanical Property, Plasticizer, Polymer Chain Scission, Polymer Degradation, Styrene-Butadiene Rubber, Thermal Aging

## 1. Introduction

The development of high-performance rubber materials is important because the purpose for the use of synthetic rubber materials is diverse. A long-term stability is demanded for rubber materials during actual use in addition to their excellent physical and mechanical properties. The surface rubber of tires, that is called tread, is the most important component that determines the total performance of a tire because it directly contacts the road surface under the application of any force. In order to satisfy the requirements as a tire tread for automobiles under harsh conditions, styrene-butadiene rubbers (SBR) have been developed. The physical properties of SBR are controlled by the composition of the styrene and butadiene units in the copolymers as well as their tacticity and regiochemical structures.[1-6] Any degradation limits the guarantee for the performance of the rubber materials for tires. In general, the degradation of rubbers includes an irreversible change in the chemical structure of the polymer chains, and their types are classified into heat, ozone, photo, chemical, radiation, mechanical, electrical, and microbial degradations based on the type of trigger.[7-13]

The degradation of rubbers involves two types of reactions. Softening-type reactions include a decrease in the molecular weight of the polymers due to the main chain scission, while the hardening-type one involves cross-linking reactions. The styrene repeating units in the SBRs are chemically stable, while the 1,2- and 1,4-butadiene units significantly participate in any reactions occurring during the thermal aging. During a hardening-type reaction, a radical abstracts hydrogen from the polymer chain. The resulting polymer radicals combine with each other, leading to cross-linking. As a result, the rubber is more hardened and becomes brittle. For the softening-type reactions, on the other hand, a carbon radical reacts with molecular oxygen. The β-scission of the main chain finally occurs via the following chain reactions, resulting in a decrease in the molecular weight.

The mechanical properties of the rubber materials depend on a change in the polymer chain structures, such as polymer chain scission and cross-linking. There are a large number of reports on the degradation behaviors of natural rubber and SBR using various analytical methods.[14-24] The structural change in the

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polymer chain and networks has been discussed for the vulcanized compounds including several additives and carbon blacks. In the present study, we investigated the mechanical properties of the SBRs during a thermal aging process. It is noted that the SBR vulcanizates were prepared without antioxidants, stabilizers, the other additives, and carbon blacks for the vulcanization process to more precisely evaluate the effect of the polymer chain structures on the mechanical properties. Furthermore, we found that the use of a nonvolatile liquid polymer as the plasticizer was valid for the maintenance of the desired mechanical properties of the SBR vulcanizate.

## 2. Experimental

### 2.1. SBR

We used the SBRs with different styrene, 1,2-, and 1,4-butadiene contents and molecular weights. The SBR samples were synthesized on a laboratory scale or commercially available. These samples included no antioxidants and stabilizers. The SBR compounds (samples A–D) consisting of a synthesized styrene-butadiene copolymer (100), a process oil (Process X-260, Japan Energy Co.) (25), stearic acid (1.25), zinc oxide (2.5), *tert*-butyl benzothiazole-2-sulfenamide as the accelerator (1.25), and sulfur (1.25) were mixed, fabricated in the shape of a sheet, and cured at 170 °C for 20 min. The values in parentheses are phr (parts per hundred rubber), i.e., the relative weight of each component. We also used the liquid type of a styrene-butadiene copolymer as the plasticizer. The formulation of the SBR vulcanizate (sample F) using the liquid polymer was as follows: a commercial styrene- butadiene copolymer (Asaprene 303, Asahi Kasei Chemicals Co.) (100), liquid styrene-butadiene copolymer (Kuraprene LSBR-820, Kuraray Co.) as the plasticizer (25), stearic acid (1.25), zinc oxide (2.1), *tert*-butyl benzothiazole-2-sulfenamide (4), and sulfur (4). The SBR vulcanizates with and without a process oil (samples E and G, respectively) were also prepared under similar conditions. Commercially available reagents were used as received without further purification.

### 2.2. Measurements

The weight-average molecular weight ($M_w$) and polydispersity ($M_w/M_n$) were determined by gel permeation chromatography (GPC) using Shimadzu RID-6A equipped with a refractive index detector and standard polystyrenes for calibration. The structure of the SBR was determined by nuclear magnetic resonance (NMR) 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. The $T_g$ values were determined as the extrapolated onset temperature of the transition, that is, the cross point of the baseline and tangent line at the maximum slope. The IR spectra were recorded using a Perkin-Elmer Auto IMAGE FT-IR spectrometer by an attenuated total reflection method.

### 2.3. Mechanical Properties

The SBR vulcanizates were sliced in order to obtain sheets with a 1-mm thickness for preparing the mechanical test pieces. The test pieces were put into an oven maintained at 100 °C for one to eight weeks, and then used for each measurement to determine the mechanical properties. The hardness was measured using an automatic hardness meter (Excel, RH-101) according to the procedure described by JIS K6253. The sample number for the hardness measurement was three, and the median value was adopted. The viscoelasticity measurement was carried out using an Iwamoto VES-F-III viscoelastic analyzer at a 12% distortion, a frequency of 10 Hz, and 25 °C, according to JIS K6394 (ISO 4664-1, 2005), in order to determine tensile complex modulus (E*) and loss angle (tanδ) values. The measurements were carried out using six test pieces and an average value and standard deviation were determined. The tensile experiment was also carried out using a Shimadzu AGS-500 apparatus, according to JIS K6251 (ISO 37, 1994 and ASTEM D624). A dumbbell-shaped sample (35 mm × 6 mm × 1 mm) was tensed at the rate of 500 mm/min, and the modulus was recorded at 300% and 100% elongations ($M_{300}$ and $M_{100}$, respectively). The median value was recorded as the $M_{300}$ or $M_{100}$ data according to a method similar to the hardness measurement.

### 2.4. Cross-Linking Density

The cross-linking density, ν (mol/mL) was calculated by the Flory-Rehner equation (Eq. 1).[25]

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

where $\nu_R$ 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 $\chi$ are the molecular volume of a solvent and the interaction parameter, respectively. In this study, we used the following values; $V_0 = 106.7$ mL, $\chi = 0.352$–$0.365$.

$$\nu_R = \frac{\text{Volume of dry polymer}}{\text{Volume of swelled polymer}} \qquad (2)$$

### 2.5. Solvent Extraction

In order 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 an 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 acetone extraction. 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. The CE fraction was analyzed by GPC measurement.

## 3. Results and Discussion

### 3.1. Sample Characterization

The polymer repeating structure of the SBR was determined on the basis of the relative intensity of the peaks due to the styrene, 1,4-, and 1,2-butadiene units, which were observed at 6.8–7.3, 5.0–5.6, and 4.7–5.0 ppm, respectively, in the $^1$H NMR spectra.[26] A typical example of the $^1$H NMR spectrum is shown in Figure 1. The $M_w$ and $M_w/M_n$ values and the $T_g$ values were determined by GPC and DSC measurements, respectively. The obtained results are shown in TABLE I. The DSC traces are shown in Figure 2. Samples A–D had relatively low styrene contents as the repeating unit (30.4–41.3%) and samples E and F had a high styrene content (68.6%). Sample C involved the highest 1,4-butadiene repeating unit (48.1%).

### 3.2. Mechanical Properties

The SBR vulcanizates (samples A–G) were heated at 100 °C for 0–8 weeks under atmospheric conditions, and the changes in the hardness, E*, tanδ, and $M_{300}$ (or $M_{100}$) values were determined. The results are summarized in TABLE II. The all values for these mechanical properties increased after the thermal aging. For example, the hardness value increased and reached the values that correspond to 1.2–1.5 times the

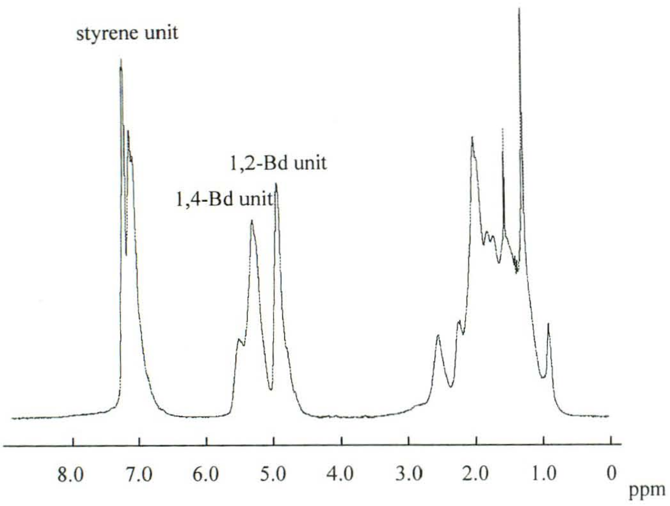

**Figure 1.** $^1$H NMR spectrum of an SBR sample (Sample A before vulcanization) in chloroform-*d* at room temperature.

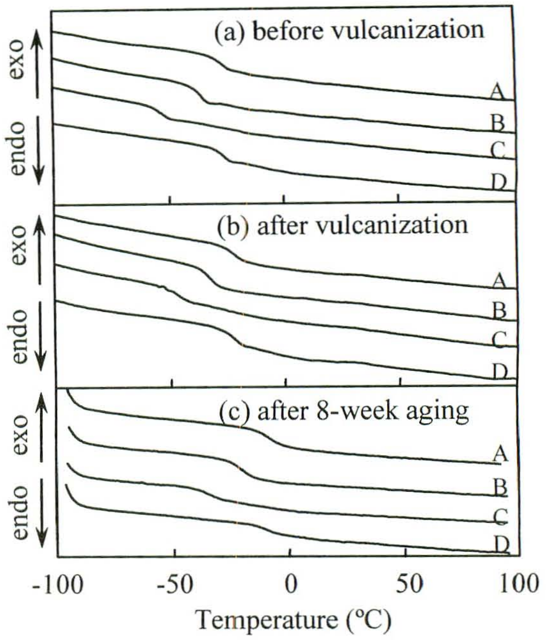

**Figure 2.** DSC traces of the SBR samples. (a) Before vulcanization, (b) after vulcanization (before aging), and (c) after 8-week aging.

**TABLE I** Characterization of Styrene-Butadiene Copolymers and the SBR Vulcanizates

| Sample code | Polymer chain structure[a] (%) (NMR) | | | $M_w$ × $10^{-6}$ (GPC) | $M_w/M_n$ (GPC) | $T_g$ (°C) (DSC) | | |
|---|---|---|---|---|---|---|---|---|
| | St | 1,2-Bd | 1,4-Bd | | | Before vulcanization | After vulcanization | After 8-week aging |
| A | 40.8 | 30.0 | 29.2 | 1.33 | 1.18 | –31.3 | –27.8 | –16.1 |
| B | 30.4 | 33.0 | 36.6 | 1.57 | 1.24 | –40.2 | –37.2 | –27.0 |
| C | 39.9 | 12.0 | 48.1 | 1.17 | 1.21 | –58.2 | –52.0 | –42.2 |
| D | 41.3 | 28.4 | 30.3 | 0.83 | 1.14 | –31.5 | –29.1 | –13.5 |
| E | 68.6 | 14.3 | 17.1 | 0.16 | 1.05 | n.d.[b] | –19.8 | –16.9 |
| F[c] | 68.6 | 14.3 | 17.1 | 0.16 | 1.05 | n.d.[b] | –14.9 | –11.5 |
| G[d] | 68.6 | 14.3 | 17.1 | 0.16 | 1.05 | n.d.[b] | –13.0 | –8.0 |

[a] St: styrene unit, 1,2-Bd: 1,2-butadiene unit, 1,4-Bd: 1,4-butadiene unit. [b] Not determined. [c] Using a liquid styrene-butadiene copolymer as the plasticizer. [d] Without plasticizers.

original one during the heating for 8 weeks. The E* values similarly increased by 1.3–2.0 times. A change in the E* and hardness values during the thermal aging is plotted in Figure 3.

The initial E* values depended on the repeating structure of the used SBRs. The E* value for sample E was the highest and changed with the largest increment during the aging, while a small change was observed

**TABLE II** Mechanical Properties of the SBR Vulcanizates before and after Thermal Aging

| Sample Code | Before Thermal Aging | | | | After Thermal Aging[a] | | | |
|---|---|---|---|---|---|---|---|---|
| | Hardness | E* (MPa) | tanδ | $M_{300}$ (MPa) | Hardness | E* (MPa) | tanδ | $M_{300}$ (MPa) |
| A | 32.9 | 2.11±0.07 | 0.471±0.035 | 1.2 | 47.8<br>(1.45) | 3.54<br>(1.68) | 0.740<br>(1.57) | 3.2<br>(2.6) |
| B | 33.1 | 1.11±0.03 | 0.145±0.015 | 1.1 | 42.2<br>(1.27) | 1.59<br>(1.43) | 0.256<br>(1.77) | 1.5<br>(1.3) |
| C | 35.5 | 1.46±0.03 | 0.207±0.015 | 1.2 | 44.3<br>(1.25) | 1.91<br>(1.31) | 0.278<br>(1.34) | 2.0<br>(1.6) |
| D | 33.6 | 2.43±0.30 | 0.745±0.056 | 1.0 | 39.9<br>(1.19) | 3.15<br>(1.30) | 0.855<br>(1.15) | 2.3<br>(2.3) |
| E | 44.5 | 3.38±0.36 | 0.550±0.014 | 1.1[b] | 68.6<br>(1.54) | 6.64[c]<br>(1.96) | 0.739<br>(1.34) | 4.5[b]<br>(4.3) |
| F[d] | 48.4 | 4.16±0.23 | 0.549±0.025 | 1.1[b] | 62.8<br>(1.30) | 6.59<br>(1.58) | 0.666<br>(1.21) | 3.2[b]<br>(2.9) |
| G[e] | 59.0 | 6.20±0.19 | 0.546±0.018 | 2.3[b] | 73.6<br>(1.25) | 12.34<br>(1.99) | 0.681<br>(1.25) | 6.9[b]<br>(3.0) |

[a] After heating at 100 °C for 8 weeks. The values in parentheses indicate the values relative to the original values before the aging. [b] $M_{100}$ value. [c] After 6 weeks. [d] Using a liquid styrene-butadiene copolymer as the plasticizer. [e] Without plasticizers.

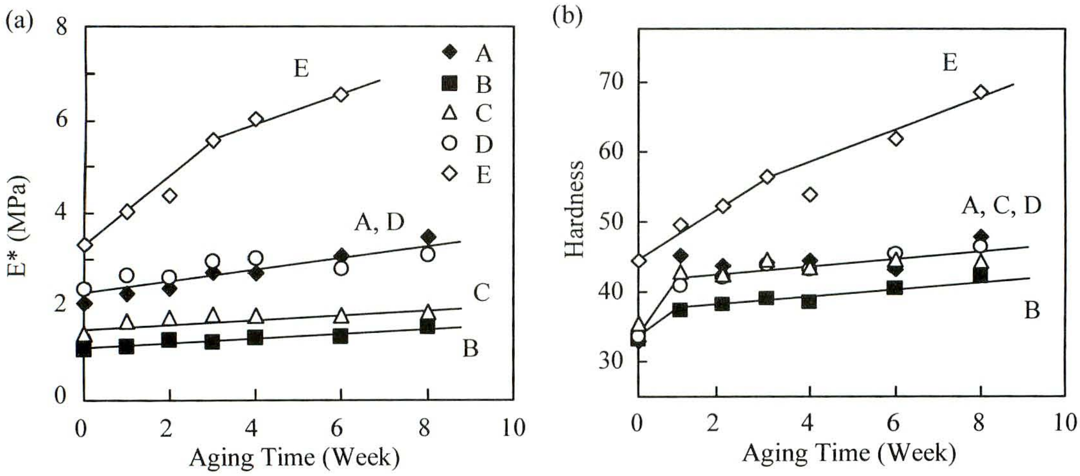

**Figure 3.** Change in the (a) E* and (b) hardness values of the SBR vulcanizates (samples A–E) during thermal aging.

for the other samples. The change in the hardness showed a similar tendency. Sample E had the largest hardness value as the initial value and the largest increment was observed during the aging. The samples A–D had a similar hardness values before aging. The hardness value for sample B became smaller than the others after the aging. For samples A–D, the hardness drastically changed during the initial aging process for 1 week. In TABLE II, the change in the tanδ and $M_{300}$ values are also shown. The tanδ values increased

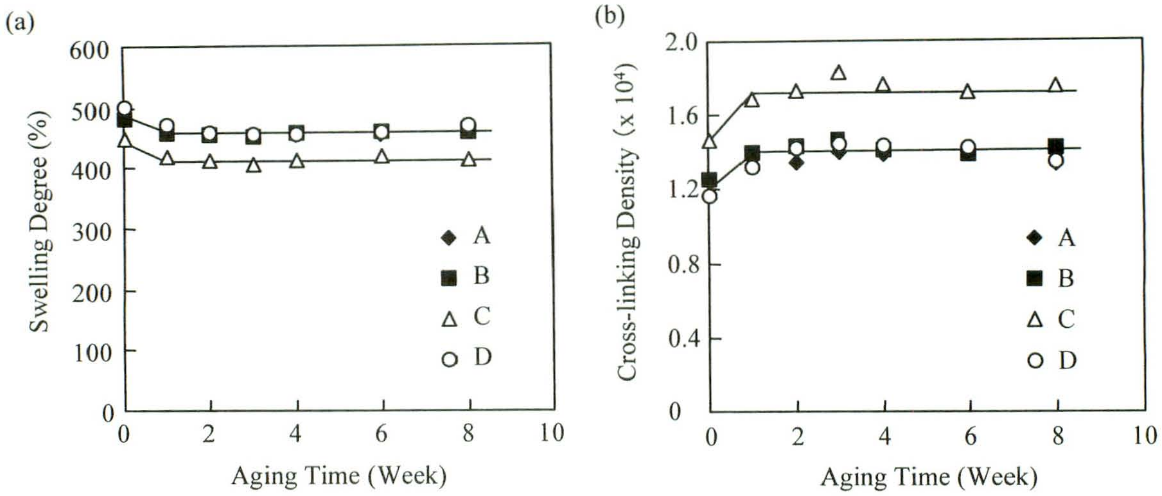

**Figure 4.** Change in (a) the degree of swelling and (b) the cross-linking density of the SBR vulcanizates (samples A–D) during the thermal aging.

during the aging and reached the values 1.1–1.8 times the original one. The all $M_{300}$ values were in the small range of 1.0–1.2 MPa before heating, but the modulus increased to 1.5–4.5 MPa in the order of E > A > D > C > B after the aging. This order agrees with the order in the E* values.

Thus, some of measurement values for the mechanical properties of the SBR vulcanizates are accounted for by considering the structure of the styrene-butadiene copolymers. The E* values increased during the thermal aging, irrespective of the amount of the styrene and butadiene units in the chain, although it was expected that the contents of the unsaturated groups would influence the hardening behavior of the SBRs. Similarly, the increase in the 1,2-butadiene content also gave high E* and tanδ values. The obtained results agree with the general expectation, that is, the SBR with a high styrene or 1,2-butadiene content is harder and has higher E* value. On the other hand, no difference was observed for the hardness and $M_{300}$ values of samples A–D as the initial values before aging. The hardness and $M_{300}$ values reflect the mechanical properties after a large deformation (300% strain for the latter). On the other hand, the E* and tanδ values were determined by the smaller deformation (12% strain). The effects of the polymer chain structure of the SBR more sensitively appear in the smaller deformation.

### 3.3. Cross-linking Reactions

The results of the DSC measurements also indicate the hardening of the SBRs after the thermal aging (Figure 2 and TABLE I). The $T_g$ values increased during the 8-week aging in the all cases. This shows a change in the polymer chain mobility by an increase in the number of cross-linking points. Therefore, we evaluated the cross-linking density ($\nu$) for the SBRs before and after the aging. The degree of swelling was used as the index for the degree of cross-linking. Figure 4(a) shows the results of the swelling measurement for each sample after thermal aging for a different time.

Before heating, sample C showed a 451% swelling, which is the lowest among all the samples; and 483–501% for the others. Sample C involves the largest 1,4-butadiene unit (48.1%). This indicates that the 1,4-butadiene repeating unit plays an important role in the vulcanization, as expected. The $\nu$ value, which was calculated on the basis of these swelling data, according to Eq. 1, is shown in Figure 4(b). As a result, sample C has the highest $\nu$ value. The major part of the cross-linking structures of the SBR is formed during the vulcanization process, but the cross-linked SBRs still contain some other reacting points. After 1 week of aging, the $\nu$ value increased by 11–15%. This is due to the formation of additional cross-linking points by the thermal aging.

**TABLE III** AE and CE Fractions and GPC Data of the SBR Vulcanizate (sample C)

| Aging Time (Week) | AE (%) | CE (%) | GPC for CE Fraction | | Relative Peak Intensity |
|---|---|---|---|---|---|
| | | | $M_w \times 10^{-4}$ | $M_w/M_n$ | |
| 0 | 21.3 | 0.1 | 2.39 | 1.47 | 0.18 |
| 2 | 20.0 | 0.1 | 2.49 | 1.55 | 0.30 |
| 4 | 19.9 | 0.2 | 2.44 | 1.64 | 0.49 |
| 6 | 19.2 | 0.4 | 2.45 | 1.71 | 0.80 |
| 8 | 19.1 | 0.6 | 2.19 | 1.75 | 1.00 |

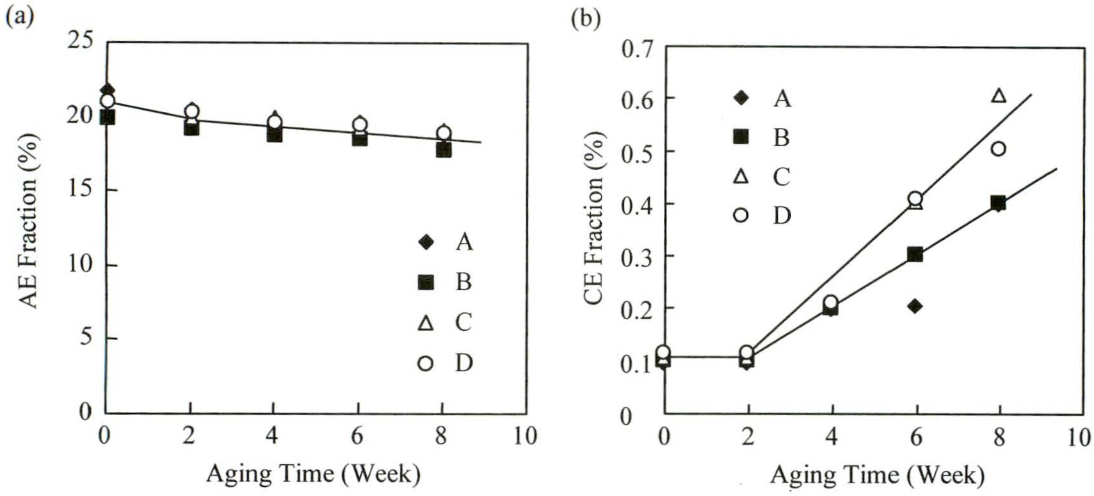

**Figure 5.** Change in the (a) AE and (b) CE fractions of the SBR vulcanizates (samples A–D) during the thermal aging.

### 3.4. Polymer Chain Scission

There is the possibility that cross-linking occurs during the thermal aging process on the one hand and the degradation of the polymer chains simultaneously occurs on the other hand. When the bond scission occurs at the branched part of the polymers, a linear free-polymer would be produced. Therefore, we carried out the two-step extraction of the soluble parts from the SBR samples using two kinds of organic solvents. First, oily and low-molecular-weight components, which were added during the vulcanization process, were extracted with acetone under reflux conditions (AE fraction). Subsequently, soluble and free polymers from the residue of the acetone extraction were then extracted with chloroform (CE fraction). The changes in the amounts of the AE and CE fractions are shown in Figure 5(a) and (b), respectively. The amount of AC fraction decreased during the thermal aging, while that of CE fraction increased.

The $M_w$ and $M_w/M_n$ values of the free polymers were determined by GPC analysis. As shown in TABLE III, the $M_w$ and $M_w/M_n$ values were (2.2–2.5) × $10^4$ and 1.5–1.7, respectively, and kept constant during the thermal aging. The $M_w$ value of the free polymers was $10^2$ times lower than the $M_w$ value (1.17 × $10^6$) for the original styrene-butadiene copolymer. An increase in the relative peak intensity of the GPC elusion curves

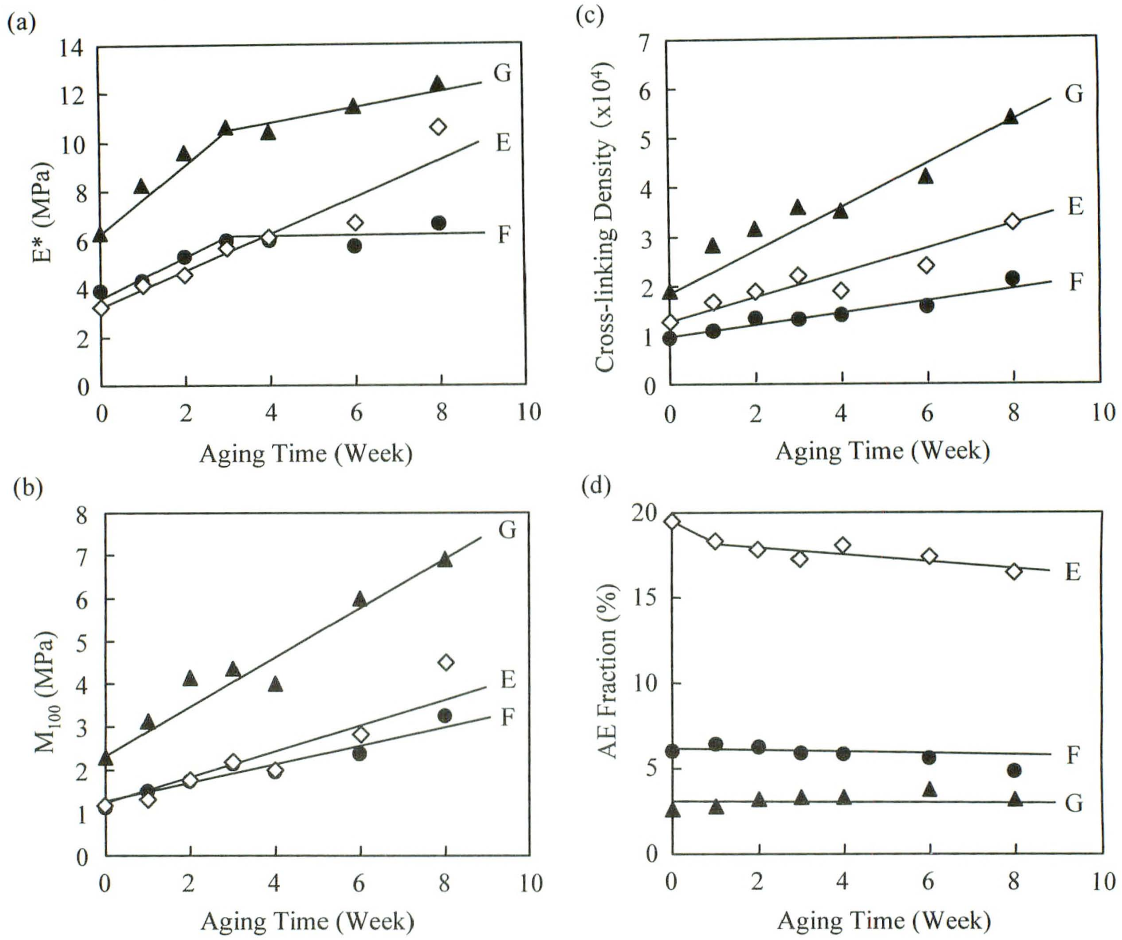

**Figure 6.** Change in the mechanical and the other properties of the SBR vulcanizates during thermal aging. (a) E*, (b) $M_{100}$ values, (c) the cross-linking density, and (d) AE fraction during the thermal aging. Plasticizer: (◊) a process oil (sample E), (•) liquid styrene-butadiene copolymer (sample F), and (▲) without plasticizers (sample G).

agrees with the fact that the CE fraction increased according to the aging time. The free polymers (CE fraction) seem to be formed irrespective of the chain structure of the polymers. In order to evaluate a change in the chemical structure of the polymer chains, the IR spectrum of the SBRs was recorded. If an oxidation reaction occurs, an absorption band due to the carbonyl group is detected. As a result, the peak due to the carbonyl group at 1730 cm$^{-1}$ was detected from the initial stage of the thermal aging, although quantitative analysis was difficult because of the small intensity of the peak.

### 3.5. Effect of Plasticizers

Moreover, we noticed a decrease in the amounts of the AE fractions during the thermal aging [Figure 5(a)]. The oily components that were added to the samples during the vulcanization process slowly vaporize during the thermal aging over a long time.[27] A constant decrease in the amount of the oily component influences the overall mechanical properties. In fact, when nonvolatile compounds as the plasticizers, such as liquid types of polybutadiene, a styrene-butadiene copolymer, and natural rubber, were used instead of the conventional process oil, we obtained the SBR vulcanizates that show the superior physical properties of during the thermal aging process. Here we show preliminary results for the mechanical properties of the SBR prepared using a liquid styrene-butadiene copolymer.[28] The SBR with a high styrene content was only used for the vulcanization using liquid polymer as the plasticizer, because the other SBRs with a low styrene content gave vulcanized samples with insufficient mechanical strength.

When the liquid styrene-butadiene copolymer was used as the plasticizer (sample F), the increase in the hardness and modulus was suppressed during the aging, as shown in TABLE II and Figure 6. This is in contrast to a large increase in the hardness, E*, and $M_{100}$ values for the cases without any plasticizer. The SBR vulcanizate was also prepared using a liquid polyisoprene as the plasticizer. The dynamic mechanical spectroscopy and DSC experiments have revealed the phase separation after vulcanization. The phase-separated structure is due to the immiscibility of the SBR and polyisoprene domains, and changed to the homogeneous structure during the aging process after 2–3 weeks. The aging behavior also changed according to the change in the phase structure. The liquid polymer chains incorporated into the SBR networks play an important role in the suppression of the polymer cross-linking, leading to the hardening of the rubber materials.

In order to examine a change in the chemical structure of the SBR vulcanizates, the observation of morphological change was attempted, but no valuable information was obtained during scanning and transmission electron microscopic observations. The rubber materials used for tires usually consist of not only polymer materials but also carbon blacks and the other inorganic materials. The dispersion and interfacial structures of carbon blacks in a polymer matrix can be observed by microscopic methods. In contrast, the SBR vulcanizates prepared in the present study imply no carbon blacks. In this case, it is difficult to detect the phase separated structure of the added polymers as the plasticizers and the SBR domains. During the thermal aging process, carbon and oxygen radicals are formed and they readily abstract hydrogens from the liquid polymer chains rather than from the SBR networks. Consequently, the cross-linking reaction between the polymer chains would be retarded. The free polymer chains are important for maintaining the stable network structure and the acceptable physical properties. The detailed results for the effects of the nonvolatile liquid polymers as the plasticizers on the properties of the SBRs are separately reported in our recent papers.[29,30]

## 4. Conclusions

The change in the mechanical properties of the SBRs with different styrene and butadiene contents and molecular weights during thermal aging was analyzed on the basis of the experimental results for the determination of the hardness and modulus values as well as the swelling and extractions experiments. During the thermal aging process, an increase in the cross-linking density of the SBRs resulted in increases in the hardness, E*, tanδ, and $M_{300}$ values. Furthermore, we also noticed the contribution of the constant evaporation of the oily component, which was added to the vulcanization process, to increases in the modulus during the long-time aging process. We demonstrated the validity of the use of nonvolatile liquid polymer as the plasticizer to obtain the desired physical properties of the SBR vulcanizates during the thermal aging.

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