

Mechanical Properties and Thermal Aging Behavior of Styrene-Butadiene Rubbers Vulcanized Using Liquid Diene Polymers as the Plasticizer

Takeo Nakazono,^{1,2} Akikazu Matsumoto²

¹Sumitomo Rubber Industry, Ltd. (SRI), 1-1-2, Tsutsui-cho, Chuo-ku, Kobe 651-0071, Japan

²Department of Applied Chemistry and Bioengineering, Graduate School of Engineering, Osaka City University, 3-3-138, Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

Received 21 July 2009; Revised 10 September 2009; accepted 10 September 2009

DOI 10.1002/app.31483

Published online 22 June 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The mechanical properties of styrene-butadiene rubber (SBR) vulcanizates prepared using various plasticizers including liquid polybutadiene and styrene-butadiene copolymers were investigated. The effect of the liquid polymers as the plasticizers on the mechanical properties of the polymers, such as the hardness, tensile storage modulus, $\tan\delta$, and the modulus at 100% elongation values, were determined before and after the thermal aging. As a result, it was revealed that the use of these liquid polymers gave less amount of change in the measurement values for the mechanical properties during the aging. The crosslinking density and the amount of free polymers were also determined on the basis of the swel-

ling and extraction data, respectively, using several organic solvents. These results support the fact that the added liquid polymers are fixed to the SBR networks. We revealed the superiority of the liquid styrene-butadiene copolymers as the plasticizer, which provides sufficient mechanical properties after vulcanization and the excellent maintenance of the properties during the thermal aging process. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 2314–2320, 2010

Key words: copolymer; crosslinking; mechanical property; liquid polymer; degradation; styrene-butadiene rubber; thermal aging

INTRODUCTION

Synthetic rubbers as high-performance rubber materials have been developed and widely used for more diverse purposes that demand excellent physical and mechanical properties and a long-term stability. The mechanical properties of rubber materials are significantly influenced by thermal and mechanical degradations during their use over a long period.^{1–7} It is well known that the degradation of rubbers induces softened- and hardened-type reactions depending on the reaction conditions.^{3–5} Softened-type reactions include a main chain scission, while the hardened-type one involves crosslinking reactions. An increase in the crosslinking density of rubbers by a radical coupling reaction leads to an increase in the hardness, modulus, and $\tan\delta$ values during thermal aging. Recently, we observed the fact that the increase in the hardness and modulus values were caused not only by the degradation of the polymer chains but also the slow evaporation of the

oily components, which were added as the plasticizer for the vulcanization process.^{8,9} When we use liquid polymers as the plasticizers, the constant performance of tires is expected for a long time due to no evaporation of the liquid polymers. In general, liquid polymers, such as liquid polybutadienes, are used as the soft segment of polyurethanes and as bonding agents and electric paints to provide tough products after solidification.^{10–17} In this study, we used liquid types of polybutadiene and styrene-butadiene copolymers as the nonvolatile plasticizers for the vulcanization process and investigated the effect of these plasticizers on the mechanical properties of the styrene-butadiene vulcanizates.

EXPERIMENTAL

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 an RI (refractive index) as the detector and standard polystyrenes for calibration. The NMR spectra were determined using a Bruker Advance II 400 spectrometer and chloroform-*d* as the solvent at room temperature.

Correspondence to: T. Nakazono (t-nakazono.az@srigroup.co.jp).

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.

Materials

The SBR compounds, which were made of a styrene-butadiene copolymer, a plasticizer, stearic acid, zinc oxide, an accelerator, and sulfur, were mixed, fabricated in the shape of a sheet, and cured at 170°C for 40 min. The formulation of the SBR vulcanizates used in this study was as follows: a styrene-butadiene copolymer (100), a plasticizer (0 or 25), stearic acid (1.25), zinc oxide (2.1), *tert*-butyl benzothiazole-2-sulfenamide as the accelerator (4), and sulfur (4). The values in parentheses are the relative weight of each component. A commercial styrene-butadiene copolymer (Asaprene 303, Asahi Kasei Chemicals) was used as the main polymer materials for the preparation of the SBR vulcanizates. A commercial liquid styrene-butadiene copolymer (Kuraprene LSBR-820, Kuraray), liquid polybutadienes (Kuraprene LBR-307 and LBR-305, Kuraray), and a process oil (X-260, Japan Energy) were used as the plasticizers. The commercially available reagents were used as received without further purification. We used no further additives and carbon blacks to more precisely evaluate the effect of the plasticizers on the mechanical properties of the SBR vulcanizates.

Mechanical properties

The SBR vulcanizates were sliced to obtain sheets with a 1-mm thickness for the preparation of the mechanical test pieces. The test pieces were put into an oven maintained at 100°C for 1–8 weeks, and then used for each measurement to determine the mechanical and the other 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 was recorded as the data. 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, to determine tensile storage modulus (E^*) and $\tan\delta$ values. The dependence of the frequency on the E^* values were checked in the frequency range of 0.05–50 Hz and no significant dependence of the frequency at the less than 10 Hz was confirmed. The measurements were carried out using 3–5 test pieces and an average value and standard deviation were determined. The tensile stress was measured using a Shimadzu AGS-500 apparatus, according to JIS K6251. A dumbbell-shaped sample was tensed at the rate of 500 mm/min, and the

modulus was recorded at a 100% elongation (M_{100}). The median was recorded as the M_{100} data according to a method similar to the hardness measurement.

Cross-linking density

The crosslinking density, ν (mol/mL), was calculated by the Flory-Rehner equation (Eq. 1).¹⁸

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

where ν_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 (Eq. 2). V_0 and χ are the molecular volume of the solvent and the interaction parameter, respectively.

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

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 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. In this study, extractions with toluene at 80°C or with tetrahydrofuran (THF) under reflux for 24 h were also carried out.

RESULTS AND DISCUSSION

Effect of plasticizers

We used the styrene-butadiene copolymer with a high styrene content as the main polymer materials for the preparation of the SBR vulcanizates in this study. The ¹H-NMR spectrum of the used styrene-butadiene copolymer is shown in Figure 1. The contents of styrene, 1,2-butadiene, and 1,4-butadiene units in the styrene-butadiene copolymer were 68.6, 14.3, and 17.1%, respectively. The M_w and M_w/M_n values were 1.56×10^5 and 1.05, respectively. Figure 1 also shows the ¹H-NMR spectra for a liquid styrene-butadiene copolymer and liquid polybutadienes as the plasticizers. The structures, the M_w and M_w/M_n values and the T_g values for the plasticizers are summarized in Table I.

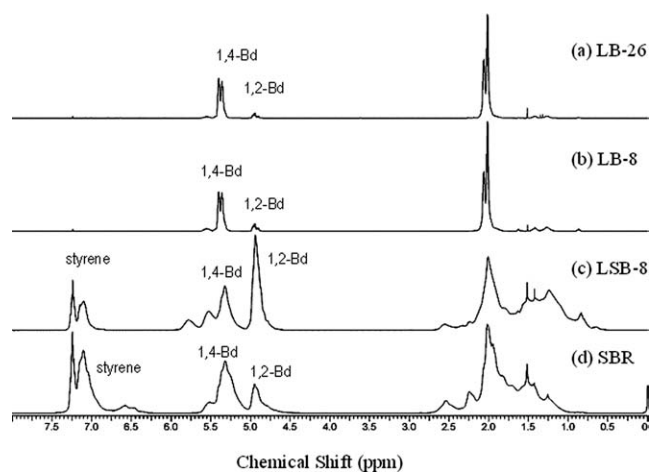


Figure 1 $^1\text{H-NMR}$ spectra of the liquid polymers and the SBR used in this study in chloroform- d at room temperature. (a) Liquid butadiene (LB-26), (b) liquid polybutadiene (LB-8), (c) liquid styrene-butadiene copolymer (LSB-8), and (d) styrene-butadiene copolymer (SBR). 1,2-Bd: 1,2-butadiene unit, 1,4-Bd: 1,4-butadiene unit.

The SBR vulcanizates I–V were prepared using different plasticizers, and then the test pieces of the SBR samples were heated at 100°C for 1–8 weeks under atmospheric conditions. Their mechanical properties were evaluated after each aging time by hardness, E^* , $\tan\delta$, and the M_{100} values. The results are shown in Figure 2 and Table II.

Among the five kinds of SBR vulcanizate samples used in this study, sample I included no plasticizer, while the others contained 18% of an oil or liquid polymer as the plasticizer. The hardness values before heating were 59.0 and 42.2–50.2 for the samples without and with plasticizers, respectively. During the heating, the hardness values for all the samples gradually increased for 8 weeks, as shown in Figure 2(a). The value reached 73.6 for sample I. Among the other samples containing plasticizers, sample II showed the largest change in the hardness value; the hardness value increased from 44.5 to 68.6 during aging. The value after aging corresponds to 1.5 times the original value. For the other three samples III–V, the hardness

increased from 42.2–50.2 before aging to 56.9–62.8 after aging and the increment was 22–35%. The change in the E^* values is shown in Figure 2(b). The E^* values also increased for all the samples during the aging process. The E^* value for sample II showed the greatest change. Similar results were also observed in the $\tan\delta$ and M_{100} values, as summarized in Table II. The M_{100} values were always high for sample I before and after aging.

The initial mechanical properties as well as their change during the thermal aging are influenced by the plasticizers. The initial values of hardness, E^* , and M_{100} values for sample I (without plasticizer) were greater than those of the others. It is noteworthy that the change in all the values of sample II, such as hardness, E^* , $\tan\delta$, and M_{100} parameters during the aging were the highest of all the values for the other samples containing a plasticizer (Table II). The initial values of hardness and E^* values for sample III (with liquid styrene-butadiene copolymer) were greater than the data for the samples with the liquid polybutadiene plasticizers due to the presence of the rigid aromatic substituent in the styrene-butadiene copolymer. The results obtained in this study agree well with the expectation that the styrene-butadiene copolymer with a high styrene content shows higher E^* and $\tan\delta$ values. The $\tan\delta$ value was dependent on the type of plasticizer. The $\tan\delta$ values for samples IV and V were lower than the others in the initial state and after aging. The effect of the molecular weight of the plasticizers were examined on the basis of the results for samples IV and V, which were prepared using the liquid polybutadienes with M_w of 11,000 and 29,000, respectively, (Table I). The higher molecular weight resulted in the highest hardness, E^* , and M_{100} values and a lower $\tan\delta$ value during the initial stage of aging. No significant effect was observed during the thermal aging by the molecular weight.

Crosslinking reactions

The SBRs undergo various changes in their chemical structures including the scission of the main chain,

TABLE I
Structure, Molecular Weight, and T_g of Plasticizers Used in This Study

Plasticizer	Structure ^a (%) (NMR)			$M_w \times 10^{-4}$ (GPC)	M_w/M_n (GPC)	T_g ($^\circ\text{C}$) (DSC)
	Styrene	1,2-Bd	1,4-Bd			
Process oil	–	–	–	–	–	–47.4
LSB-8	14.2	32.8	53.0	1.11	1.04	–18.4
LB-8	–	12.3	87.7	1.12	1.06	–97.0
LB-26	–	8.8	91.2	2.91	1.02	–96.1

^a 1,2-Bd, 1,2-butadiene unit; 1,4-Bd, 1,4-butadiene unit.

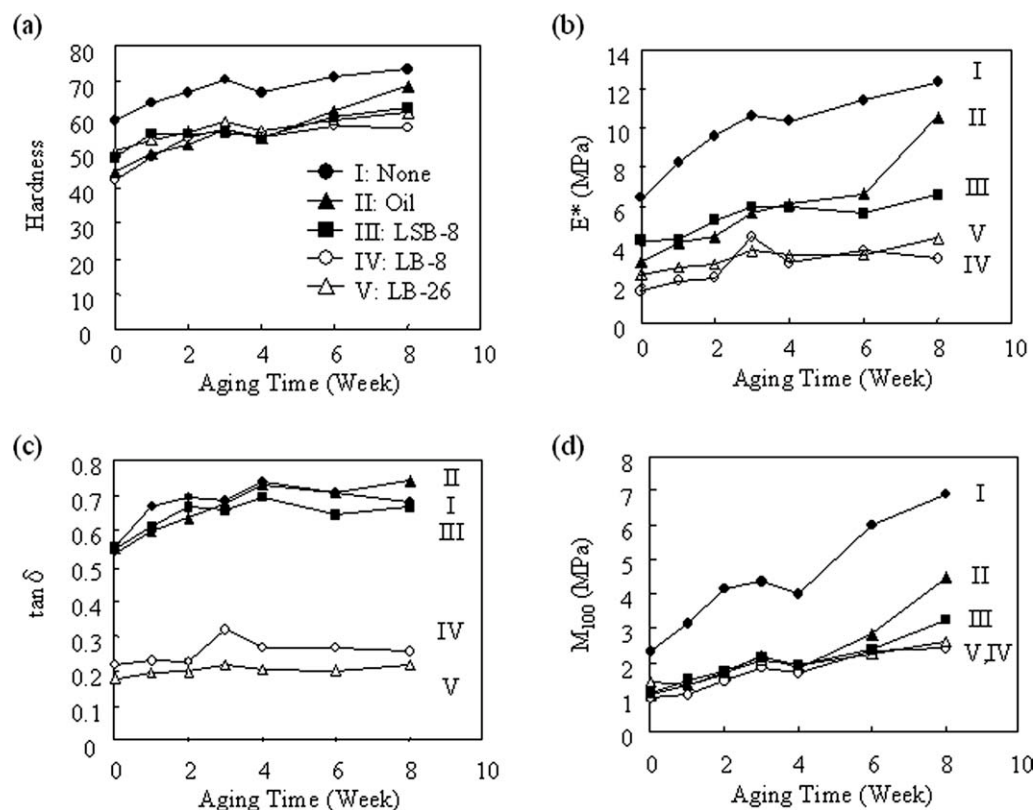


Figure 2 Change in the mechanical properties of the SBR vulcanizates I-V during the thermal aging. (a) Hardness, (b) E^* , (c) $\tan\delta$, and (d) M_{100} values.

crosslinking, and the oxidation reaction upon heating. The selectivity of these reactions depends on the temperature and atmospheric conditions.^{4,5} The changes in the mechanical properties observed in this study were primarily induced by the crosslinking reactions during the thermal aging. The results of the DSC measurements of the SBR vulcanizates indicate the hardening of the rubbers after the aging. The T_g values increased by 3–15°C during the 8-week aging, as shown in Table II. Next, we eval-

uated the crosslinking density for the SBRs before and after the aging. The degree of swelling was used as the index for the degree of crosslinking. Figure 3(a) shows the results of the swelling measurement for each sample after the thermal aging for a different time.

Before heating, samples I and II showed an ca. 400% swelling, which is lower than the other samples using the liquid polymers. During the vulcanization process, the liquid polymers were reacted and

TABLE II
Mechanical Properties of SBR Vulcanizates Before and After Thermal Aging^a

Sample Code	Aging (Week)	Hardness	E^* (MPa)	$\tan\delta$	M_{100} (MPa)	T_g (°C)
I	0	59.0	6.20 ± 0.19	0.546 ± 0.018	2.30	-13.0
	8	73.6 (1.25)	$12.34 (1.99)$	$0.681 (1.25)$	6.91 (3.00)	-8.0
II	0	44.5	3.38 ± 0.36	0.550 ± 0.014	1.05	-19.8
	8	68.6 (1.54)	$10.56 (3.12)$	$0.739 (1.34)$	4.46 (4.25)	-16.9
III	0	48.4	4.16 ± 0.23	0.549 ± 0.025	1.12	-13.1
	8	62.8 (1.30)	$6.59 (1.58)$	$0.666 (1.21)$	3.24 (2.89)	-9.5
IV	0	42.2	1.87 ± 0.17	0.207 ± 0.012	0.97	-37.5
	8	56.9 (1.35)	$3.29 (1.76)$	$0.256 (1.24)$	2.40 (2.47)	-32.7
V	0	50.2	2.71 ± 0.11	0.175 ± 0.008	1.44	-46.3
	8	61.2 (1.22)	$4.40 (1.62)$	$0.219 (1.25)$	2.61 (1.81)	-31.5

^a Values in parentheses are relative values versus those before aging.

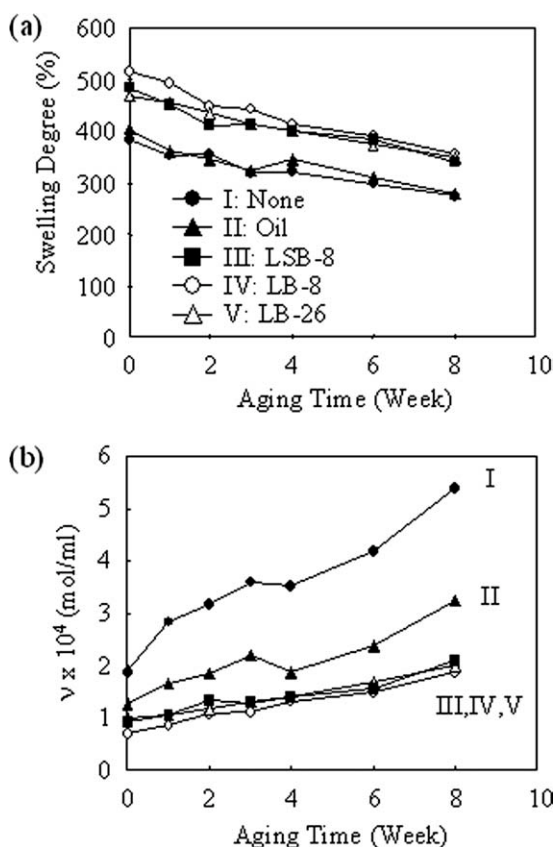


Figure 3 Change in (a) the degree of swelling and (b) the crosslinking density of the SBR vulcanizates I–V during the thermal aging.

connected to a part of the SBR networks. The presence of relatively low-molecular-weight liquid polymers may result in a decrease in the average density of the crosslinking points in the network structures of the SBRs. The reason why the density of the crosslinking points decreased in the presence of the liquid polymers is a decrease in the relative amount of the sulfur added for vulcanization. For all the samples, the degree of swelling decreased during the heating for 8 weeks. A change in the crosslinking density, which was calculated on the basis of these swelling data, according to Eq. 1, is shown in Figure 3(b). The crosslinking structures of the SBR are first formed during the vulcanization process, and the network structure of the SBRs further changed by the additional crosslinking reactions during the thermal process. Sample I has the highest value of the crosslinking density before heating, because it includes no plasticizer as the diluent material. Sample II had the highest crosslinking density among the samples with plasticizers. The crosslinking density values of samples I and II increased during the aging. In contrast, samples III–V using the liquid polymers showed only a slight increase in the crosslinking density values. The crosslinking reactions

seemed to be apparently suppressed during the aging process when the liquid polymers were used as the plasticizers. This is due to no increase in the crosslinking points of the SBR networks when the liquid polymers react with the SBRs. The liquid polymers are supposed to be connected to the networks as the dangling chains.

Uptake of liquid polymers into networks

We carried out the extraction of the soluble parts from the SBR samples after the aging using two kinds of organic solvents to investigate the amount of the free polymers included in the SBRs. First, the oily and low-molecular-weight components, which were added during the vulcanization process, were extracted with acetone under reflux conditions as the AE fraction. Subsequently, the soluble and free polymers were extracted using chloroform from the residue obtained after the acetone extraction. The extracts were isolated as the AE and CE fractions after evaporating the solvents. The changes in the amounts of the AE and CE fractions are shown in Figure 4.

The AE fraction for sample II was much greater than the others, as expected. This is because the process oil added for the vulcanization is readily extracted by acetone. Interestingly, samples III–V with the liquid polymers showed only 1–2% as the CE fraction, although the added liquid polymers must be extracted by chloroform. Actually, however, the amount of the extracted free polymers was much lower than the expected one based on the amount of the used liquid polymers during the vulcanization process. We further checked the extraction amounts using hot toluene boiling at 80°C and THF under reflux conditions. As shown by the results in Figure 5, the extraction amount with the hot toluene and THF of samples I–V were similar to the total amounts of the AE and CE fractions. These results indicate that the low-molecular-weight compounds and the free polymers contained in the SBR after vulcanization were quantitatively extracted, independent of the type of solvents used.

Judging from the amounts of the extracted polymers, it is considered that the added liquid polymers reacted with the SBR and were connected to the SBR as a part of the network structures during the vulcanization process. The unreacted liquid polymer (free polymer) still remained as the plasticizer in the SBR vulcanizates and it may further react during the thermal aging. It is assumed that polymer degradation accompanying chain scission may occur during the aging, but the crosslinking reaction simultaneously takes a role in the suppressed formation of free polymers.

In Figure 5, the amount of the extracted fraction was much low for sample V. This is due to the effect of the molecular weight of the used liquid polymers. The higher the molecular weight of the liquid polymers added as the plasticizer, the more frequent the reaction of the liquid polymer to make a covalent bond connected to the SBR networks. The experimental results obtained in this study suggest that the reactive liquid polymers are very useful for the vulcanization process as the plasticizers and these liquid polymers also act as the trapping agent of the free radicals formed during the thermal aging. The liquid polymers act as the antioxidant agent for the SBR networks during the thermal aging process, leading to the constant mechanical properties during their use. If a chain scission occurs during the thermal aging process, free polymers with a shorter chain length are produced. However, the extraction data shown in Figure 4 indicate a continuous decrease in the amount of the extracted fractions during the thermal aging. This suggests small contribution of chain scission to produce a free polymer during the thermal aging process under the conditions used in this study.

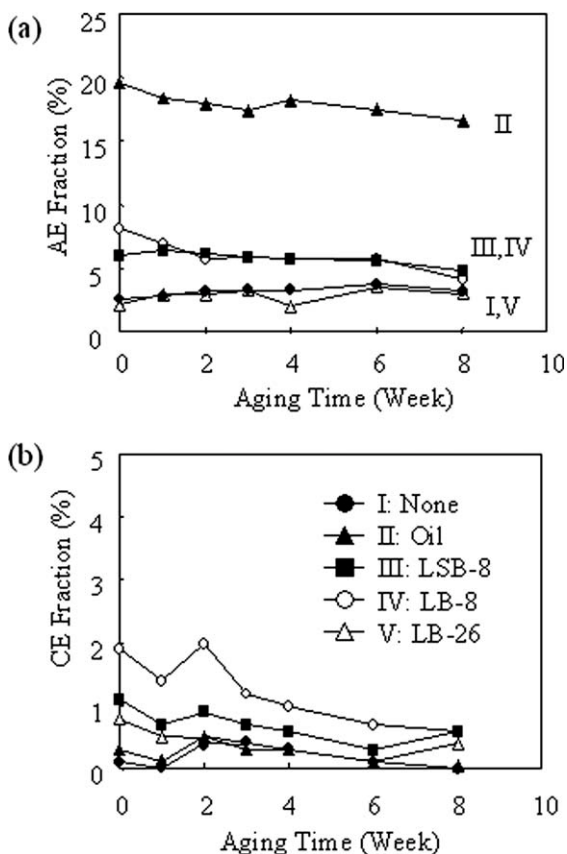


Figure 4 Change in the (a) AE and (b) CE fractions of the SBR vulcanizates I-V during the thermal aging.

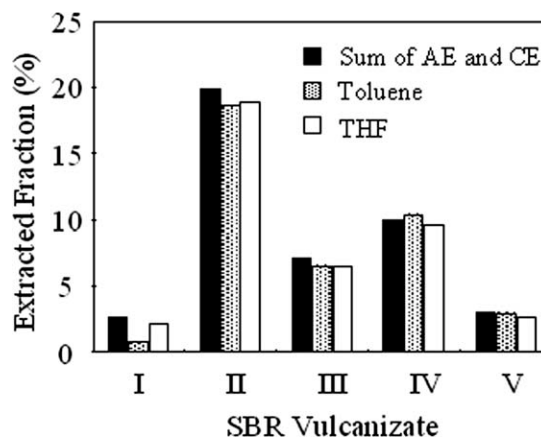


Figure 5 Extracted fractions of the SBR vulcanizates I-V before aging. Extracted with acetone, chloroform, and THF under reflux for 24 h, and toluene at 80°C for 24 h.

CONCLUSIONS

We carried out the thermal aging testing of several kinds of SBR vulcanizates prepared using a conventional process oil and liquid types of a styrene-butadiene copolymer and polybutadienes as the nonvolatile plasticizers. The changes in the structure and mechanical properties of the SBR vulcanizates during the thermal aging were analyzed on the basis of the results for the hardness, tensile storage modulus, $\tan\delta$, and the modulus at 100% elongation values determination as well as the swelling test. The process oil slowly evaporated during the heating, and it changed the mechanical properties of the SBR. In contrast, constant mechanical properties were observed during the thermal aging when the liquid polymers were used as the plasticizers for the vulcanization process, as shown in an illustrative conclusion in Figure 6. Especially, the mechanical properties

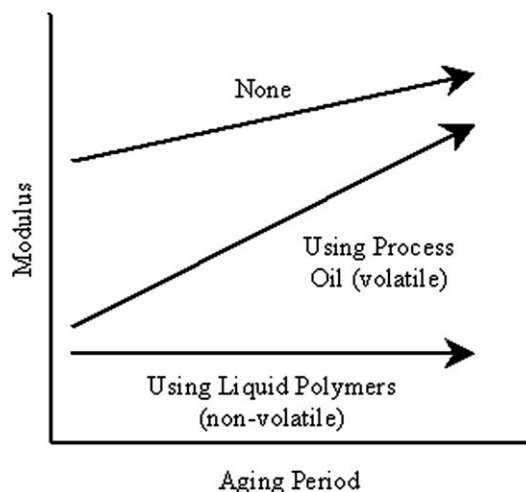


Figure 6 Illustrative conclusion for the effect of the addition of liquid polymers as the plasticizers to the SBR vulcanizates.

of the sample using the liquid styrene-butadiene copolymer were acceptable because the values of a variety of mechanical properties are similar to those for the sample with a conventional process oil in the initial state before the thermal aging. Furthermore, the protecting effect of the network structures of the SBRs by the liquid polymers was also observed and it led to the constant mechanical properties during their use. Thus, it has been revealed that the liquid polymers are superior as the plasticizer because they provide the excellent maintenance of the properties during the thermal aging process.

References

1. Schnabel, W. *Polymer Degradation: Principles and Practical Applications*; Hanser: Munchen, 1981.
2. Li, G.-Y.; Koenig, J. L. *Rubber Chem Technol* 2005, 78, 355.
3. Saito, T. *J Soc Rubber Ind Jpn* 1995, 68, 284.
4. Ahagon, A.; Kida, M.; Kaidou, H. *Rubber Chem Technol* 1990, 63, 683.
5. Kaidou, H.; Ahagon, A. *Rubber Chem Technol* 1990, 63, 698.
6. Santoso, A.; Giese, U.; Schuster, R. H. *Rubber Chem Technol* 2007, 80, 762.
7. Ellwood, K. R. J.; Baldwin, J.; Bauer, D. R. *Rubber Chem Technol* 2006, 79, 249.
8. Nakazono, T.; Matsumoto, A. *J Appl Polym Sci*, submitted.
9. Kataoka, T.; Zetterlund, P. B.; Yamada, B. *Rubber Chem Technol* 2003, 76, 507.
10. Goodman, C.; Li, S. L.; Albrecht, R. M.; Cooper, S. L. *Macromolecules* 1988, 21, 2367.
11. Yang, C. Z.; Hwang, K. K. S.; Cooper, S. L. *Macromol Chem Phys* 1983, 184, 651.
12. Rath, S. K.; Ishack, A. M.; Suryavansi, U. G.; Chandrasekhar, L.; Patri, M. *Prog Org Coat* 2008, 62, 393.
13. Ajaz, A. G. *Rubber Chem Technol* 1995, 68, 481.
14. Millett, J. C. F.; Bourne, N. K.; Akhavan, J. *J Appl Phys* 2004, 95, 4722.
15. Gupta, D. C.; Divekar, P. K.; Phadke, V. K. *J Appl Polym Sci* 1997, 65, 355.
16. Bandgar, B. M.; Krishnamurthy, V. N.; Mukundan, T. Sharma, K. C. *J Appl Polym Sci* 2002, 85, 1002.
17. Piorkowska, E.; Argon, A. S.; Cohen, R. E. *Polymer* 1993, 34, 4435.
18. Flory, P. J.; Rehner, J., Jr. *J Chem Phys* 1943, 11, 521.