

Phase Separation and Thermal Aging Behavior of Styrene-Butadiene Rubber Vulcanizates Using Liquid Polymers as Plasticizers Studied by Differential Scanning Calorimetry and Dynamic Mechanical Spectroscopy

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ABSTRACT: Styrene-butadiene rubber (SBR) vulcanizates were prepared using plasticizers including the four liquid types of styrene-butadiene copolymers (LPSB), polybutadiene (LPB), polyisoprene (LPI), and the hydrogenated polyisoprene (LHPI) as well as the conventional process oil, and their phase-separated structures and mechanical properties were investigated by differential scanning calorimetry and dynamic mechanical spectroscopy. The phase separation was observed for the SBR vulcanizates when LPI and LHPI were used as the plasticizers, while the LPSB and LPB gave homogeneous structures because of the good miscibility with the SBR. The phase-separated structure of

the SBR vulcanizate prepared using LPI changed to the homogeneous during the thermal aging. We revealed the role of the liquid polymers as the plasticizers in maintaining the physical and mechanical properties of the SBR vulcanizates during the thermal aging process when the plasticizers were miscible to the SBR. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 434–440, 2011

Key words: copolymer; differential scanning calorimetry; dynamic mechanical spectroscopy; mechanical property; liquid polymer; miscibility; phase separation; styrene-butadiene rubber; thermal aging

INTRODUCTION

High-performance synthetic rubbers have been developed 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 time period. On the other hand, the physical properties of polymer blends and composites significantly change depending on their phase-separated structures.^{1–6} Block and graft copolymers are often used as the compatibilizer for the mutual immiscible components of a polymer blend system in order to modify the physical properties of the materials. Dynamic vulcanization is also used for the production of high-performance rubber materials with the desired properties and a long-term stability.⁷

The degradation of rubbers induces softening and hardening-type reactions, which involve a main chain scission and cross-linking reactions, respectively.^{8–13} The reaction pathway depends on the polymer structure and the reaction conditions. An increase in the cross-linking density of rubbers by a radical coupling reaction leads to an increase in the hardness and brittleness during the aging process. It was previously pointed out that an increase in the hardness and modulus of styrene-butadiene rubber (SBR) vulcanizates was caused by not only 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.^{14,15} In fact, when liquid polybutadiene (LPB) and liquid styrene-butadiene copolymers (LPSB) were used, the good performance of tires was achieved due to no evaporation of these liquid polymers as the plasticizers.¹⁴

More recently, we found that the liquid polyisoprene (LPI) can also be used as the good plasticizer, but the thermal aging behavior was more complex and different from the results for the cases using LPB and LPSB.¹⁶ Furthermore, we noticed that the liquid hydrogenated polyisoprene (LHPI) showed less suppression effect for hardening the SBR during the thermal aging process. In this study, we

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investigated the miscibility of the SBR and the added plasticizers by differential scanning calorimetry (DSC) and dynamic mechanical spectroscopy (DMS). We revealed the important role of the miscibility of the SBR and the liquid polymers in the maintenance of the physical properties of the SBR vulcanizates.

EXPERIMENTAL

Materials

The SBR compounds, which were made of a styrene-butadiene copolymer (100), a liquid polymer as the plasticizer (25), stearic acid (1.25), zinc oxide (2.1), *tert*-butyl benzothiazole-2-sulfenamide as the accelerator (4), and sulfur (4), were mixed, fabricated in the shape of a sheet, and cured at 170°C for 40 min. The values in parentheses are phr (parts per hundred of rubber). A commercial styrene-butadiene copolymer (Asaprene 303, Asahi Kasei Chemicals Co.) was used as the main component for the preparation of the SBR vulcanizates. A commercial LPSB (Kuraprene LSBR-820, Kuraray Co.), LPB (Kuraprene LBR-307 and LBR-305, Kuraray Co.), LPI (Kuraprene LIR-30, Kuraray Co.), and LHPI (Kuraprene LIR-200, Kuraray Co.) were used as the plasticizers. The contents of styrene, 1,2-butadiene, and 1,4-butadiene units in the used styrene-butadiene copolymer as the main component were 68.6, 14.3, and 17.1%, respectively. The weight-average molecular weight (M_w) and polydispersity (M_w/M_n) values were 1.56×10^5 and 1.05, respectively. In this study, we used no further additives and carbon blacks in order to more precisely evaluate the effect of the plasticizers on the mechanical properties of the SBR vulcanizates. The commercially available reagents were used as received without further purification.

The SBR vulcanizates were sliced in order 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.

Measurements

The M_w and M_w/M_n values were determined by gel permeation chromatography (GPC) using a Shimadzu RID-6A equipped with a refractive index detector and standard polystyrenes for calibration. The nuclear magnetic resonance (NMR) spectra were determined 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 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 dynamic mechanical properties were determined using a Seiko DMS-6100 dynamic mechanical analyzer under atmospheric conditions. The polymer sheets were cut into sample sizes of 20 mm × 10 mm × 1 mm for the DMS measurement. The measurements were carried out using the tensile mode at the frequencies of 0.05–50 Hz and the heating rate of 1 or 2°C/min in the temperature range of –150 to 100°C. The dependence of the frequency on the storage modulus (E') and loss angle ($\tan\delta$) values were checked at 25°C in the frequency range of 0.05–50 Hz. The measurements were carried out using three to five test pieces and an average value was determined. The temperature dependence was determined at a frequency of 1 Hz.

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 3, and the median value was adopted. 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 × 6 mm × 1 mm) was tensed at the rate of 200 mm/min, and the modulus was recorded at 100% elongation (M_{100}). 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 3, and the median values were recorded.

Cross-linking density and solvent extraction

The cross-linking density, ν (mol/mL), was calculated by the Flory-Rehner equation, according to the method previously described.^{14,17} The volume fraction of the polymer after swelling 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. In order to isolate the soluble fractions of the SBR samples, successive two-step extractions were carried out using acetone and chloroform for 24 h under reflux conditions. The total extracted fraction was determined as the sum of the weight fractions obtained each extraction.

RESULTS AND DISCUSSION

We used four kinds of commercial liquid polymers, LPSB, LPB, LPI, and LHPI. Their repeating structure, M_w and M_w/M_n values, and T_g values were determined by NMR, GPC, DSC measurements, respectively. The results are shown in Table I. After the vulcanization, a phase-separated structure was observed when LPI and LHPI were used as the

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

Plasticizer	Structure (%) (NMR)			$M_w \times 10^{-4}$ (GPC)	M_w/M_n (GPC)	T_g (°C) (DSC)
	Styrene	1,2-Diene	1,4-Diene			
LPSB	14.2	32.8	53.0	1.11	1.04	-18.4
LPB	-	12.3	87.7	1.12	1.06	-97.0
LPI	-	6.6	93.4	3.26	1.18	-67.2
LHPI	ca.100% hydrogenation of LPI			3.72	1.23	-64.7

plasticizers. On the other hand, LPSB and LPB gave the homogeneous SBR vulcanizates. The phase separation was confirmed by the DSC and DMS measurements. Figure 1 shows DSC traces for the SBR vulcanizates, which prepared using LPSB, LPI, and LHPI as the plasticizers, or without a plasticizer.

The SBR vulcanizate obtained using LPSB showed a T_g at -14.9°C , similarly to that for the vulcanizate prepared without any plasticizer ($T_g = -14.1^\circ\text{C}$) before the thermal aging. The T_g value linearly increased to -8.5°C during the 8-week aging period because of the occurrence of the additional cross-linking reactions of the polymer chains when no

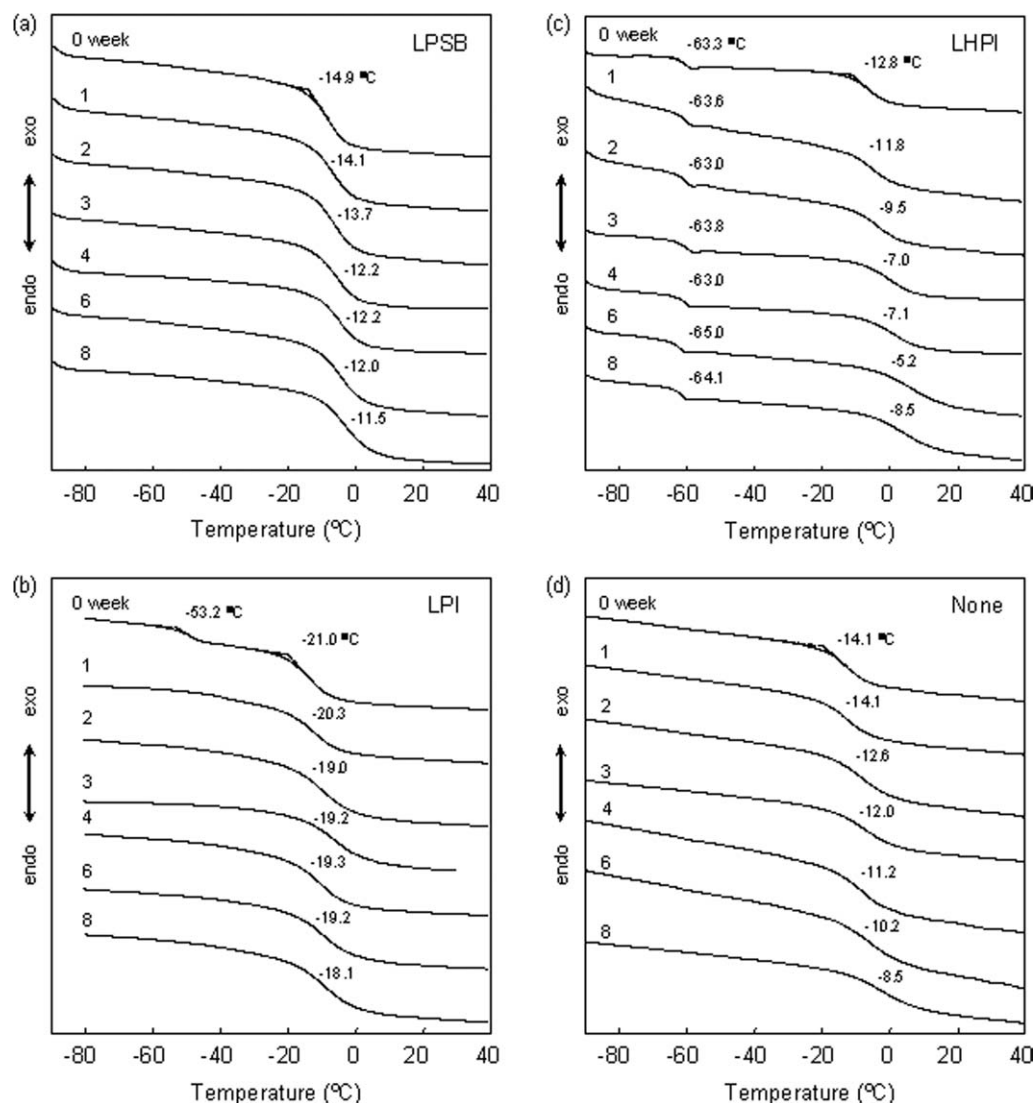


Figure 1 Change in the DSC traces for the SBR vulcanizates prepared using liquid polymers as the plasticizers during the thermal aging process for 8 weeks: (a) LPSB, (b) LPI, (c) LHPI, and (d) without plasticizers. Heating rate of $10^\circ\text{C}/\text{min}$ in a nitrogen stream.

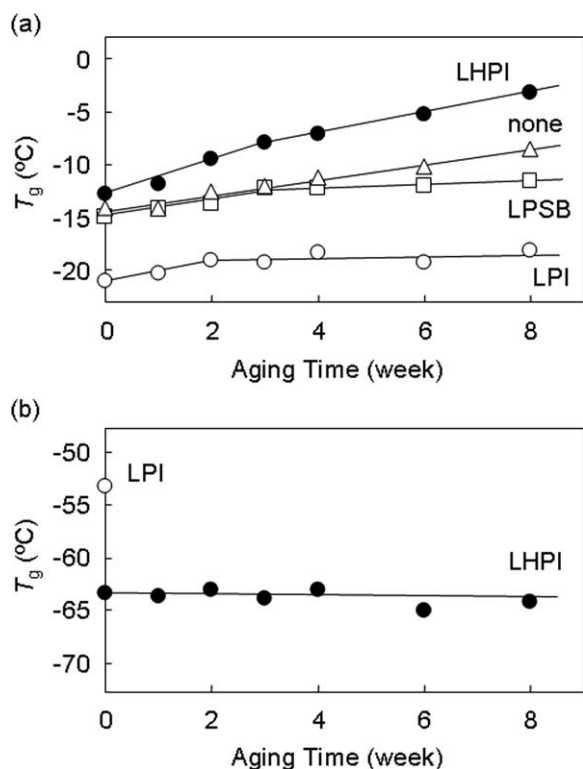


Figure 2 Change in the T_g values of the SBR vulcanizates prepared using liquid polymers as the plasticizers during the thermal aging process, determined by DSC at the heating rate of 10°C/min. (a) For the SBR phase and (b) the liquid polymer phase: (□) LPSB, (○) LPI, (●) LHPi, and (△) without plasticizers.

plasticizer was used. The change in the T_g values for each SBR vulcanizates versus the thermal aging period is plotted in Figure 2. In the case using LPSB, the T_g value increased during the initial 3 weeks in a fashion similar to the behavior of the SBR without a plasticizer, but no further increment was observed and the constant T_g value was obtained after the 4-week aging period. This result suggests that the LPSB chains acted as the inhibitor for an increase in the number of the cross-linking points involved in the SBR networks.

On the other hand, the T_g due to LPI domain was detected at -53.2°C before the thermal aging in addition to the T_g at -21.0°C due to the SBR in the vulcanizates. This indicates that the immiscibility of LPI and SBR resulted in the presence of the phase-separated LPI domains in the whole SBR vulcanizates. Interestingly, the LPI domain disappeared after the thermal aging. Namely, the initial phase-separated structure changed to the homogeneous structure after the thermal aging for 1–2 weeks. The saturated hydrocarbon polymer LHPi, which was synthesized by the quantitative hydrogenation of LPI, resulted in the phase-separated SBR vulcanizates, irrespective of the thermal aging period. This result was different from the result for the case

using LPI. As shown in the change in the T_g values in Figure 2, the T_g due to the both domains of the LHPi and the SBR were observed at -63 and -13°C, respectively, before the aging. The T_g values for each domain were -64 and -3°C, respectively, after 8-week aging. Thus, no change in the T_g values for the LHPi domain was observed during the aging, while a large increase was observed for the T_g value for the SBR domain. The increasing behavior of the T_g value for the phase-separated SBR domain was similar to a result for the SBR prepared without a plasticizer. This is due to the complete immiscibility of the LHPi chains with the SBRs.

The phase-separated structure and some mechanical properties were alternatively investigated by the DMS measurement. First, in order to examine the dependence of the applied frequency, the E' and $\tan\delta$ data were collected at various frequencies in the range of 0.05–50 Hz at 25°C. Figure 3 shows the plots for the frequency dependence of the values for the SBR vulcanizates prepared with LPSB, LPB, and a process oil as the plasticizers, or no plasticizer. The relatively moderate dependency was observed in a region at 0.05–10 Hz, independent of the kind

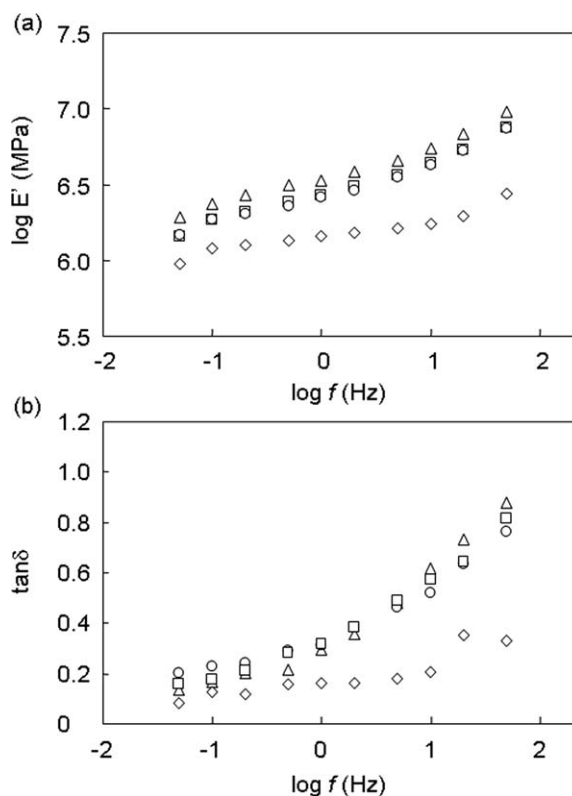


Figure 3 Frequency dependence of (a) tensile storage modulus (E') and (b) $\tan\delta$ values in the frequency range of 0.05–50 Hz for the SBR vulcanizates prepared using liquid polymers as the plasticizers: (○) LPSB, (◇) LPB, (□) a process oil, and (△) without plasticizers. The DMS measurement was carried out at 25 °C

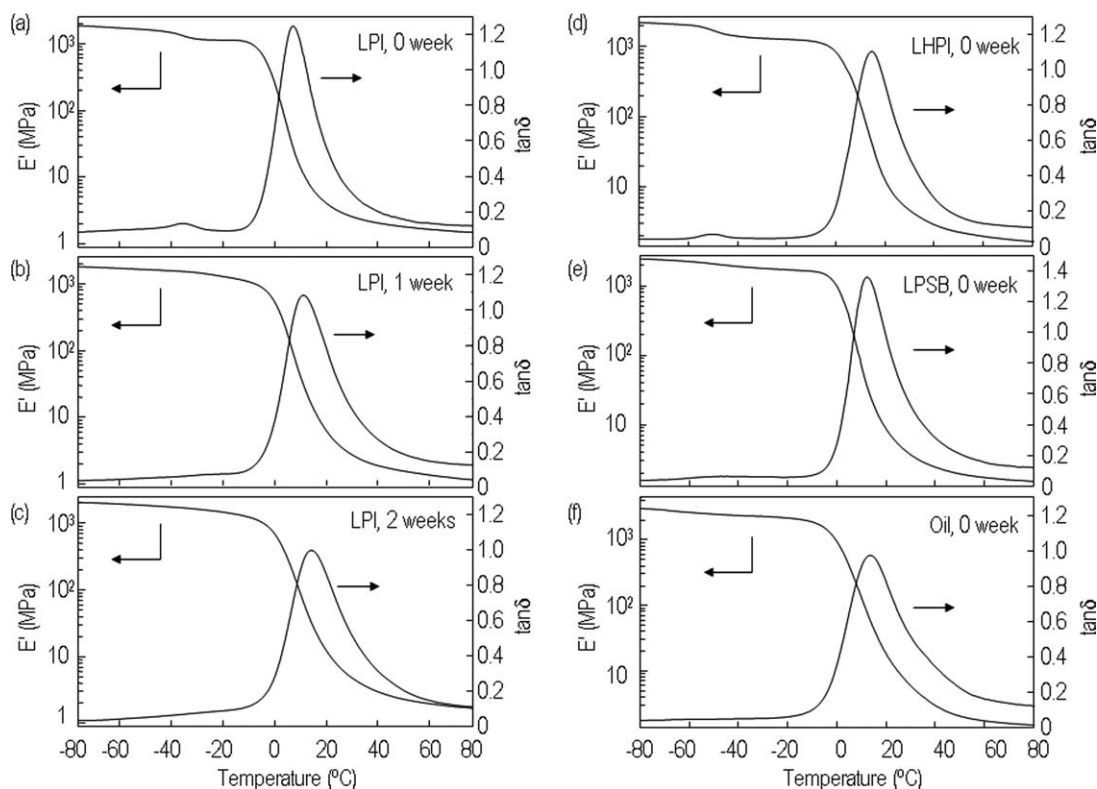


Figure 4 Temperature dependences of tensile storage modulus (E') and $\tan\delta$ values for the SBR vulcanizates using liquid polymers as the plasticizer before and after the thermal aging, determined by DMS measurement at a frequency of 1 Hz. Plasticizer and aging time: (a) LPI, 0 week, (b) LPI, 1 week, (c) LPI, 2 weeks, (d) LHPI, 0 week, (e) LPSB, 0 week, and (f) a process oil, 0 week.

of the plasticizers. The E' values of the SBR vulcanizates using LPSB were similar to those for the SBR using a conventional process oil, and slightly smaller than those without a plasticizer. The LPB has the lowest T_g value among the liquid polymers used in this study (see Table I), and therefore, the obtained SBR vulcanizate also showed the lowest hardness and modulus values. The plateau values were observed for the SBR using LPB in the wide range of 0.1–10 Hz region. A similar frequency dependence was also observed for the plots of the $\tan\delta$ values, as shown in Figure 3(b). Next, we further investigated the temperature dependence of the E' and $\tan\delta$ values in the temperature range of -150 to 100°C at the heating rate of 1 or $2^\circ\text{C}/\text{min}$. The typical results for the SBR vulcanizates under various conditions (plasticizer and aging time) are shown in Figure 4. In this figure, the changes in the temperature range from -80 to 80°C are shown.

For the SBR vulcanizate using LPI as the plasticizer, the E' value decreased at approximately -30 and 10°C in the two steps when the temperature increased. The peaks were observed at -35.5 and 7.1°C in the $\tan\delta$ plots. This clearly indicates the phase separation of the LPI and SBR phases at the initial stage of the aging. After 1-week aging, the dual $\tan\delta$ peaks due to the phase-separated structure was not

observed. This result from the DMS measurements agreed well with the result from the DSC analysis (Figure 1). In Table II, the E' and $\tan\delta$ values observed at 25°C are shown, together with the peak temperature and intensity of the $\tan\delta$ values. The dual $\tan\delta$ peaks were also observed when LHPI was used as the plasticizer. Single $\tan\delta$ peak was observed for the all other cases. For the SBR using LPI, the change in these values during the thermal aging process is also summarized in Table II. The E' value determined at 25°C increased from 3.04 to 12.57 MPa during the 6-week aging process. Similarly, the $\tan\delta$ value also increased from 0.408 to 0.716. The $\tan\delta$ peak temperature increased from 7.1 to 16.7°C when the aging period became longer. This suggests a significant change in the dynamics of the whole SBR vulcanizates after the transformation of the phase structure from the phase-separated to the homogeneous one. On the other hand, it is speculated that the local mobility of the polymer chains has no change during the aging process, considered on the basis of the constant T_g values determined by DSC, as already described.

We further evaluated the effects of the used plasticizers and the aging time on the mechanical and structural properties of the SBR vulcanizates. Table III summarizes the results for several mechanical and physical properties of the SBRs prepared using

TABLE II
DMS Data at the Frequency at 1 Hz for the SBR Vulcanizates Prepared Using Liquid Polymers as the Plasticizers

Plasticizer	Aging time (weeks)	Data at 25°C		tanδ peak data	
		E' (MPa)	tanδ	Temperature (°C)	Intensity
LPSB	0	5.26	0.751	12.7	1.345
LPI	0	3.04	0.408	-35.5, 7.1	0.133, 1.273
	1	4.76	0.520	11.1	1.096
	2	7.10	0.674	14.3	1.004
	4	9.96	0.696	14.8	0.972
	6	12.57	0.716	16.7	0.849
LHPI	0	6.20	0.677	-49.9, 14.4	0.085, 1.190
Process oil	0	9.11	0.648	13.4	1.011

various plasticizers before and after the thermal aging, such as the hardness, modulus at the 100% elongation (M_{100}), the strength (σ_b) and the extension ratio (λ_b) at the tensile breaking point, and the cross-linking density (ν). These are typical parameters for the evaluation of the properties of rubbery materials.^{14,18}

When the initial mechanical properties of the SBRs prepared using various plasticizers were compared, all the SBRs have similar values for the hardness (42.2–49.4), M_{100} (0.97–1.47 MPa), and σ_b (5.81–11.86 MPa) values. These values were smaller than those for the SBR without any plasticizer: hardness = 59.0, M_{100} = 2.30 MPa, and σ_b = 13.13 MPa. The SBR using LPB had the lowest hardness and modulus values among the SBR using the liquid polymers as the plasticizers, while that prepared using LHPI had the highest values. During the thermal aging, hardness, M_{100} , and ν values increased according to the length of the thermal aging period. The λ_b values decreased with

an increase in the aging time and achieved a quarter or half of the original value. The σ_b values tended to increase during the thermal aging, but they included a large experimental error. This is because the breaking of the sample is a macroscopic event, and the breaking point is determined by the characteristics of the weakest area in the samples. As a result, the σ_b values after the thermal aging process were in a wide range of 0.80–1.5 times of the original values. The amount of the soluble components was almost constant to be 2–7%, being much smaller than the values for the SBR using a process oil (16.6–20.1%). Totally, the SBR vulcanizate fabricated using LPSB had the most superior and stable properties. The mechanism for the suppression of the degradation of the SBR networks during the thermal aging process is speculated as follows.

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

TABLE III
Mechanical Properties of SBR Vulcanizates before and after Thermal Aging^a

Plasticizer	Aging (weeks)	Hardness	M_{100} (MPa)	σ_b (MPa)	λ_b (%)	$\nu \times 10^4$ (mol/mL)	Extracted fraction (%)
LPSB	0	48.4	1.12	11.86	484	0.93	7.1
	4	54.6 (1.1)	1.94 (1.7)	15.26 (1.3)	400 (0.83)	1.40 (1.5)	6.4 (0.90)
	8	62.8 (1.3)	3.24 (2.9)	11.87 (1.0)	231 (0.48)	2.10 (2.3)	5.5 (0.77)
LPB	0	42.2	0.97	5.81	315	0.99	3.0
	4	56.2 (1.3)	1.93 (2.0)	6.93 (1.2)	275 (0.87)	1.42 (1.4)	2.3 (0.77)
	8	56.9 (1.4)	2.40 (2.7)	7.15 (1.2)	204 (0.65)	1.99 (2.0)	3.5 (1.2)
LPI	0	48.4	1.19	9.57	462	0.72	4.1
	4	58.3 (1.2)	3.25 (2.7)	7.63 (0.80)	194 (0.42)	1.40 (2.5)	4.6 (1.1)
	8	72.0 (1.5)	3.21 ^b (2.7) ^b	14.59 (1.5)	121 (0.26)	4.38 (6.1)	3.9 (0.95)
LHPI	0	49.4	1.47	10.88	420	0.84	3.8
	4	65.7 (1.3)	3.83 (2.6)	14.68 (1.3)	235 (0.56)	1.54 (1.8)	4.4 ^b (1.2) ^b
	8	72.8 (1.5)	7.47 (6.9)	11.40 (1.1)	149 (0.35)	2.28 (2.7)	3.7 (0.97)
Process oil	0	44.5	1.05	8.90	435	1.28	20.1
	4	53.8 (1.2)	1.83 (1.6)	11.97 (1.3)	337 (0.78)	1.87 (2.1)	18.5 (0.92)
	8	68.6 (1.5)	2.80 ^b (2.7) ^b	10.98 (1.2)	190 (0.44)	3.24 (2.5)	16.6 (0.83)
None	0	59.0	2.30	13.48	344	1.88	2.7
	4	66.9 (1.1)	4.00 (1.7)	13.13 (0.97)	256 (0.74)	3.52 (1.9)	3.6 (1.3)
	8	73.6 (1.2)	6.91 (3.0)	16.11 (1.2)	177 (0.51)	5.38 (2.9)	3.2 (1.2)

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

^b After 6-week aging.

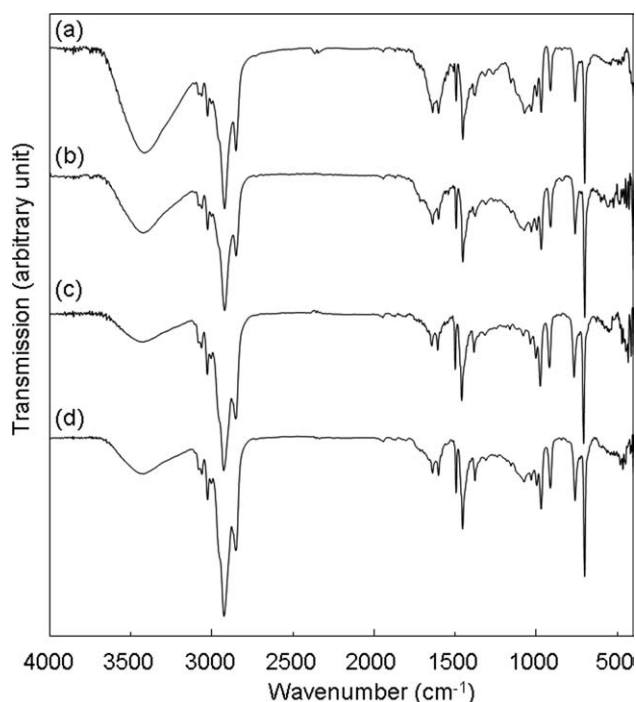


Figure 5 IR spectra of the SBR vulcanizates fabricated using LPI and LHPI as the plasticizers before and after the thermal aging. Plasticizer and aging time: (a) LPI, 0 week, (b) LPI, 2 weeks, (c) LHPI, 0 week, and (d) LHPI, 2 weeks.

examine a change in the chemical structure of the SBR vulcanizates, IR spectra were recorded before and after the thermal aging, as shown in Figure 5. As a result, however, no change was observed in each spectrum for the SBR prepared using LPI and LHPI as the plasticizers after 2-week aging. Any morphological change was also attempted to be observed, but no valuable information was obtained during SEM and TEM 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 this study imply no carbon blacks. In this case, it is difficult to detect the phase separated structure of the LHPI (or LPI) and SBR domains by SEM and TEM observations. The miscible liquid polymer chains probably diffuse into the whole SBR vulcanizates. 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. A part of LPI was phase-separated from the SBR domain and the others are incorporated in the SBR networks. The free LPI chains gradually diffuse and react for connection to the SBR networks during the

aging. On the other hand, LPSB and LPB are highly miscible to the SBR and the remaining free LPSB and LPB chains are present in the SBR domain, while some of LPSB and LPB chains are incorporated in the SBR network. The free LPSB and LPB chains are important for maintaining the stable network structure and the constant physical properties. The dangling short chain can also show a similar effect.

CONCLUSION

We revealed that liquid polymers can be used as the plasticizer instead of a volatile process oil for the vulcanization of the SBR and that the physical properties of the SBR vulcanizates kept constant during the thermal aging, for example, constant T_g and modulus values. The process oil slowly evaporated during the heating, and it changed the mechanical properties of the SBR during use. In contrast, the constant mechanical properties were observed during the thermal aging when the liquid polymers were used as the plasticizers for the vulcanization process. Especially, LPSB showed the most excellent properties as the plasticizer for the SBR vulcanizates because it gave desired mechanical properties at the initial stage as well as stable properties during the thermal aging process. We have pointed out that the miscibility of the liquid polymers and SBR is important for maintaining the physical properties during the thermal aging on the basis of the results of the DSC and DMS experiments for the SBR vulcanizates using LPI and LHPI as the plasticizers.

References

1. Utracki, L. A. *Polymer Alloys and Blends, Thermodynamics and Rheology*; Carl Hanser: Munich, 1989.
2. Gupta, R. K.; Kennel, E.; Kim, K.-J. *Polymer Nano Composites Handbook*; CRC Press: Boca Raton, 2010.
3. Okay, O. *Prog Polym Sci* 2000, 25, 711.
4. Lodge, T. P. *Macromol Chem Phys* 2003, 204, 265.
5. Balazs, A. C.; Emrick, T.; Russell, T. P. *Science* 2006, 314, 1107.
6. Lynd, N. A.; Meuler, A. J.; Hillmyer, M. A. *Prog Polym Sci* 2008, 33, 875.
7. Inoue, T. *Prog Polym Sci* 1995, 20, 119.
8. Li, G. -Y.; Koenig, J. L. *Rubber Chem Tech* 2005, 78, 355.
9. Saito, T. *J Soc Rubber Ind Japan* 1995, 68, 284.
10. Ahagon, A.; Kida, M.; Kaidou, H. *Rubber Chem Tech* 1990, 63, 683.
11. Kaidou, H.; Ahagon, A. *Rubber Chem Tech* 1990, 63, 698.
12. Santoso, A.; Giese, U.; Schuster, R. H. *Rubber Chem Tech* 2007, 80, 762.
13. Ellwood, K. R. J.; Baldwin, J.; Bauer, D. R. *Rubber Chem Tech* 2006, 79, 249.
14. Nakazono, T.; Matsumoto, A. *J Appl Polym Sci* 2010, 118, 2314.
15. Kataoka, T.; Zetterlund, P. B.; Yamada, B. *Rubber Chem Tech* 2003, 76, 507.
16. Nakazono, T.; Ozaki, A.; Matsumoto, A. *Chem Lett* 2010, 39, 268.
17. Flory, P. J.; Rehner, J., Jr. *J Chem Phys* 1943, 11, 521.
18. Nakazono, T.; Matsumoto, A. *J Appl Polym Sci*, in press (DOI 10.1002/app.33150).