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Effect of Phase Separation on Thermal Aging Behavior of Styrene–Butadiene Rubber Vulcanizates Using Liquid Polyisoprene as Plasticizer

Takeo Nakazono,*[1,2] Anri Ozaki,[2] and Akikazu Matsumoto*[2]
[1]*Sumitomo Rubber Industry, Ltd. (SRI), 1-1-2 Tsutsui-cho, Chuo-ku, Kobe 651-0071*
[2]*Department of Applied Chemistry and Bioengineering, Graduate School of Engineering, Osaka City University,*
3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585

(Received December 11, 2009; CL-091104; E-mail: t-nakazono.az@srigroup.co.jp, matsumoto@a-chem.eng.osaka-cu.ac.jp)

Styrene–butadiene rubber (SBR) vulcanizates were prepared using liquid polyisoprene (PI) and hydrogenated polyisoprene (HPI) as the plasticizers, and their structure and mechanical properties were investigated. The effect of the phase-separated structures of the SBR and the liquid polymers on the mechanical properties of the SBR vulcanizates was investigated. The constant physical properties were observed for the SBR vulcanizates during the thermal aging process when SBR and the plasticizer were miscible with each other in the vulcanizates.

The physical properties of polymer blends and composites significantly depend on the phase-separated structures.[1–6] Compatibilizers, such as block and graft copolymers, are used to modify the miscibility and physical properties of the polymer blends. Dynamic vulcanization is also used for the production of high-performance rubber materials, which have the desired physical and mechanical properties and a long-term stability.[7] On the other hand, the mechanical properties of rubber materials are significantly influenced by the thermal and mechanical degradations during their use over a long time period.[8–13] The degradation of rubbers induces softening- and hardening-type reactions, which involve a main chain scission and cross-linking reactions, respectively. The reaction pathway depends on the polymer structure and the reaction conditions. An increase in the crosslinking density of rubbers by a radical coupling reaction leads to an increase in the hardness and modulus values during the aging process.

It was previously pointed out that increased hardness and modulus were 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 vulcanization process.[14,15] In fact, when liquid polybutadiene and styrene–butadiene copolymers were used as the plasticizers, good tire performance was achieved for a long time due to no evaporation of these liquid polymers.[14] Polyisoprene (PI) is also a candidate for plasticizer because PI has a low glass transition temperature (T_g) and excellent properties as the soft segment for rubber materials. In this study, we used liquid-PI and hydrogenated PI (HPI) as the nonvolatile plasticizers for a vulcanization process and investigated the effect of these plasticizers on the mechanical properties of the SBR vulcanizates. We revealed an important role for the miscibility of the SBR and the liquid polymers on maintaining the constant physical properties of the SBR vulcanizates during aging.

The SBR compounds consisting of a commercial styrene–butadiene copolymer (100), PI (1,4-*cis*-isoprene repeating unit 93.4%, 3,4-isoprene repeating unit 6.6%, $M_w = 2.8 \times 10^4$) or HPI (ca. 100% hydrogenation of PI, $M_w = 3.1 \times 10^4$) 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 the relative weight of each component. The contents of styrene, 1,2-butadiene, and 1,4-butadiene units in the used copolymer as the main component 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. 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.

A phase-separated structure was observed for the SBR vulcanizates when PI and HPI were used as the plasticizers in this study, in contrast to the homogeneous structure observed for the SBR vulcanizates using liquid polybutadiene and styrene–butadiene copolymer in a previous study.[14] The phase separation was confirmed by differential scanning calorimetry (DSC) measurements and dynamic mechanical spectroscopy (DMS). Figure 1 shows the T_g for the SBR vulcanizates using the PI and HPI, determined by DSC and DMS. The T_g's due to PI and HPI domains were detected at −53 and −63 °C, respectively, before thermal aging in addition to the T_g's at −21 and −13 °C due to the SBR in the vulcanizates. This indicates that the immiscibility of PI or HPI in the SBR results in the formation of PI and HPI domains phase-separated from the whole SBR vulcanizates. Interestingly, the PI domain vanished after a 1-week thermal aging at 100 °C. The change in the initial phase-separated structure to the homogeneous structure after the thermal aging

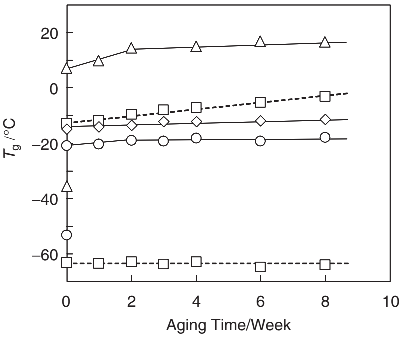

Figure 1. Change in T_g values of the SBR vulcanizates during thermal aging at 100 °C. (○) Determined by DSC for the SBR prepared using PI, (□) by DSC for the phase-separated SBR prepared using HPI, and (△) determined from tan δ data at 1 Hz by DMS for the SBR prepared using PI. (◇) Determined by DSC for the homogeneous SBR prepared using the liquid styrene–butadiene copolymer.

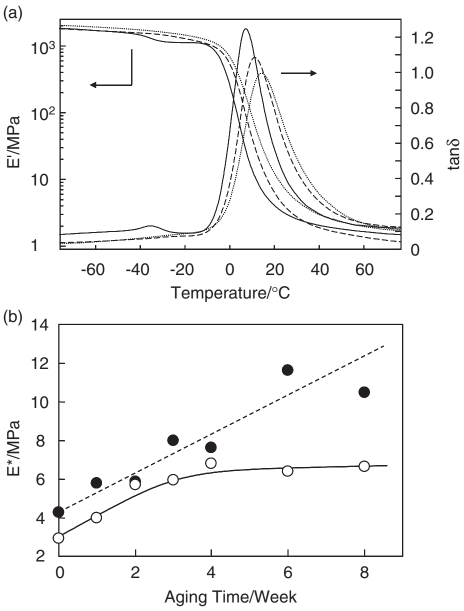

Figure 2. (a) Temperature dependences of tensile storage modulus (E') and tan δ values for the SBR vulcanizates using PI as the plasticizer before and after the thermal aging at 100 °C, determined by DMS measurement at a frequency of 1 Hz. Aging time: (—) 0, (– –) 1, and (- - -) 2 weeks. (b) Change in the tensile complex modulus (E^*) value of the SBR vulcanizates using PI (○) and (●) HPI as the plasticizer during thermal aging at 100 °C, determined by DMS measurement at a frequency of 10 Hz and 25 °C.

for 1–2 weeks was alternatively confirmed by the DMS measurement, as shown in Figure 2a. The T_g data based on the tan δ at a frequency of 1 Hz gave a similar conclusion, as shown in Figure 1.

Furthermore, we found that the T_g value remained constant for the homogeneous SBR systems using PI during the thermal aging process after 2 weeks. On the other hand, the T_g value of the SBR domain increased when the heterogeneous structure was formed in the case using HPI. The T_g value for the homogeneous SBR vulcanizate prepared using PI was lower than that for the SBR domain of the phase-separated vulcanizate using HPI. This is due to a difference in the miscibility of the PI and HPI chains with the SBR. The PI chains incorporated into the SBR networks play an important role in the surpression of the polymer crosslinking, leading to the hardening of the rubber materials. A carbon radical formed during the thermal aging readily abstracts a hydrogen at the allyl position of the dangling and short PI chains ($M_w = 3 \times 10^4$) rather than from the styrene–butadiene copolymers chain of the SBR networks. Consequently, the crosslinking reaction between the polymer chains would be retarded.

The effect of the PI chains homogeneously incorporated into the SBR networks also affected other physical properties, such as the complex modulus (E^*), modulus at 100% elongation, and hardness, which are typical parameters for the evaluation of the modulus of rubbery materials. The results for the E^* values are shown in Figure 2b. The E^* value increaseed during the initial thermal aging process (within 2 weeks) for the SBR using PI, and during the entire aging period of the SBR using HPI. Again, the importance of the homogeneous dispersion of the plasticizers in the SBR vulcanizates was demonstrated. Figure 3 shows a schematic illustration for the change in the SBR network structures from the phase-separated to the homogeneous during the thermal aging process. The PI chains diffuse and react for connection to the SBR networks during the aging.

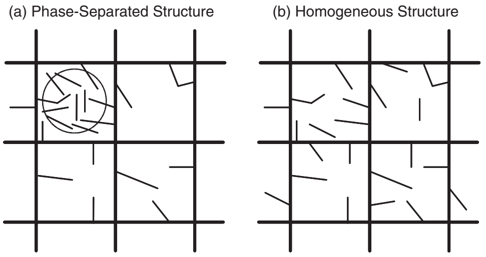

Figure 3. Schematic illustration of the phase-separated (a) and homogeneous (b) structures of the SBR vulcanizates fabricated using PI as the plasticizer. The thick and thin lines indicate the SBR networks and PI chains, respectively.

Thus, we successfully showed that liquid polymers can be used as the plasticizer instead of a volatile process oil for the vulcanization of SBR. The process oil slowly evaporated during the heating, and it changed the mechanical properties of the SBR during use. In contrast, constant mechanical properties were observed during the thermal aging when the liquid polymers were used as the plasticizers for the vulcanization process. Especially, the miscibility of the liquid polymers and SBR is important for maintaining the physical properties, such as constant T_g and modulus values during the thermal aging.

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