Tear energy and strain-induced crystallization of natural rubber/styrene-butadiene rubber blend

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Abstract. Strain-induced crystallization of natural rubber (NR), dispersed in styrene-butadiene rubber (SBR), was investigated in relation to dimensional feature of a dispersoid and crosslink density of NR by measuring tear energy (G) of crosslinked NR/SBR blends. The crosslinked NR/SBR blends in ratios of 1/9 and 3/7 by weight were prepared by mixing masticated NR and SBR with an internal mixer at a rotor speed of 30 rpm, followed by crosslinking with dicumyl peroxide on a hot press at 444 K for 60 min. The G, measured in wide-ranges of temperature and tear rate, was superposed into a master curve with a Williams-Landel-Ferry shift factor. The G of the NR/SBR(3/7) blend abruptly decreased to a level comparable to that of SBR at about melting temperature of NR crystals formed on straining. The temperature, at which the dramatic decrease in the G occurred, was associated with the dimensional feature of the NR dispersoid and the crosslink density.

1. Introduction
Crystallization of a minor component as a dispersoid is of great importance to control mechanical properties of rubbery multi-component system, i.e. rubber blend. It has been anticipated that the crystallization of the minor component such as a crystallizable rubber improves tensile strength and tear strength of the major amorphous rubber as a matrix. However, little work has been studied on an effect of the crystallization of the minor crystallizable rubber on the properties of the major amorphous rubber. Thus, it is necessary to investigate the crystallization of the minor crystallizable rubber in the rubber blend and its effect on the mechanical properties of the major amorphous rubber.

Finely-divided material is widely recognized to crystallize more slowly because a probability of finding a suitable crystal nucleus in small volumes of the materials is quite low. For example, the crystallization of natural rubber (NR) in latex, the particle size of which was less than 1 μm in diameter, was suppressed at -29 °C by a factor of at least 10 times in comparison with the bulk material.[1] In contrast, our previous study demonstrated that the rapid crystallization due to heterogeneous nucleation occurred at -25 °C when the average diameter of the NR particle was longer than about 1 μm.[2] These suggest that the crystallization of NR is dependent upon the dimensional

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feature of the particle. It is, thus, interesting to investigate a relationship between the particle dimension and the mechanical properties, since the outstanding mechanical properties are closely related to the strain-induced crystallization.

Recently, we proposed a novel method[3] to investigate the strain-induced crystallization of NR, which was a measurement of tear energy (\(G\)) of the NR/styrene-butadiene rubber (SBR) blend, since the strain-induced crystallization plays an important role in preventing crack growth of the blend under large deformation.[4] The \(G\) of the NR/SBR blend was superposed into two curves with a Williams-Landel-Ferry (WLF) shift factor, whereas the \(G\) was superposed into a single master curve, as in the previous works.[5] The difference in the \(G\) between the NR/SBR blend and the SBR was assumed to be due to the strain-induced crystallization of NR.

In this study, the effects of dimensional feature and crosslink density on the \(G\) of the crosslinked NR/SBR blend were investigated to prove the strain-induced crystallization of NR in the blend. The NR/SBR blend was crosslinked with dicumyl peroxide. The morphology of the blend was observed by transmission electron microscopy. The principle of time-temperature superposition was applied to make the master curve of the \(G\) of the blend over wide ranges of temperature and tear rate.

2. Experimental
NR used in this study was prepared by coagulation of commercial high-ammonia natural rubber latex (Golden hope) followed by drying at 50 °C for a week under reduced pressure. SBR was kindly supplied from Nippon Zeon Co., Ltd. (Nipol1502). NR was masticated with an internal mixer (TOYO SEIKI SEISAKU-SYO, Ltd.) at a rotor speed of 30 rpm for 15 min. The masticated NR was mixed with SBR in ratios of 3/7 (NR/SBR(3/7) blend) and 1/9 (NR/SBR(1/9) blend) by weight for 20 min. Dicumyl peroxide (DCP, PERCUMYL D-40(NOF CORPORATION)) was added to the blends, and then they were cured on a hot press at 444 K for 60 min. The crosslink density was estimated in terms of the Flory-Rehner equation[6] from swelling ratios determined with benzene and \(n\)-heptane, respectively.[7]

Morphological observation for the NR/SBR(3/7) and NR/SBR(1/9) blends was performed with a JEOL (Tokyo, Japan) JEM-2100 at an accelerating voltage of 200 kV. The ultrathin section of the blends was prepared with an ultramicrotome equipped with a REICHERT-NISSEI ULTRACUT N below 200 K. The section was stained with RuO₄.

The tear strength (\(G\)) was measured with trousers-type strips at various temperatures and tear rates. A specimen used was prepared according to the previous method.[3] The tear rate (\(R\)) was defined as a mean value for the crosshead speed of the testing machine.

| Sample          | Crosslink density × 10⁴ (mol cm⁻³) |
|-----------------|-----------------------------------|
|                 | NR phase | SBR phase |
| NR/SBR(3/7)     | 0.913     | 1.24      |
| NR/SBR(1/9)     | 0.826     | 1.02      |
| H-NR/SBR(3/7)   | 2.76      | 3.69      |

3. Results and Discussion
Crosslink density of NR/SBR blends, estimated by the following Flory-Rehner expression,[6] is tabulated in Table 1:

\[
v = \frac{S_B + \chi_B S_B^2 + \ln(1 - S_B)}{V_B (S_B^{1/3} - S_B / 2)} = \frac{S_H + \chi_H S_H^2 + \ln(1 - S_H)}{V_H (S_H^{1/3} - S_H / 2)}
\]
where \( \nu, S, V \) are the crosslink density of the rubber, the volume fraction of the rubber in the swollen specimen, and the molar volume of the solvent, respectively; the subscripts represent the solvents used, i.e., benzene and \( n \)-heptane. The values of interaction parameters (\( \chi \)) between the rubber and the solvents were referred to the literatures.[8,9] The estimated value of the crosslink density of the NR-phase in each blend was almost similar to that of the SBR phase. The value was independent of the composition of the blend; that is, the value of the NR/SBR(3/7) blend was identical to that of the NR/SBR(1/9) blend. The value of the H-NR/SBR(3/7) blend was about 3 times as large as that of the NR/SBR(3/7) blend.

Figure 1 (a) and (b) show TEM images for NR/SBR(1/9) blend and NR/SBR(3/7) blend, respectively. The bright domain is corresponding to NR-rich phase and dark domain is to SBR-rich phase, since the blends were stained with RuO\(_4\). As for the NR/SBR(1/9) blend, the NR domain of less than 1 \( \mu \)m in diameter was dispersed into the SBR matrix, in which the geometrical feature of the NR-domain as a dispersoid was spherical, as in the case of ordinary immiscible polymer blends. In contrast, for the NR/SBR(3/7) blend, the feature of the NR dispersoid was ellipsoidal rather than spherical and its diameter was much longer than that of the NR/SBR(1/9) blend. The ellipsoidal feature of the NR domains may be explained to be due to an unsatisfied mechanical mixing.

Figure 2 shows the \( G \) of NR/SBR(3/7) and NR/SBR(1/9) blends, which are represented as filled and open symbols, respectively. The solid line corresponds to a master curve of \( G \) of SBR superposed with a shift factor. The \( G \) of the NR/SBR(1/9) blend was in good agreement with that of SBR. In contrast, the \( G \) of the NR/SBR(3/7) blend was larger than that of SBR itself, represented as a solid line. Furthermore, the \( G \) of the NR/SBR(3/7) blend was divided into two curves: one for the \( G \) measured at 273 and 278 K and the other at temperatures ranging from 298 to 333 K, whereas the \( G \) of the NR/SBR(1/9) blend was not; i.e. the single master curve. The abrupt increase in the \( G \) of the NR/SBR(3/7) blend may be attributed to a reinforcing effect of the strain-induced crystals of NR dispersoid as a filler.

The effect of the crosslink density of NR on the \( G \) of the NR/SBR blend was investigated with the NR/SBR(3/7) and H-NR/SBR(3/7) blends. Figure 3 shows the master curves of the \( G \) of the NR/SBR(3/7) and H-NR/SBR(3/7) blends, which are represented as open and filled symbols, respectively. The \( G \) of the H-NR/SBR(3/7) blend was well-superposed to each other to make a single master curve, which was distinguished from the \( G \) of the NR/SBR(3/7) blend. This demonstrates that the strain-induced crystallization of NR dispersoid is suppressed by crosslinking, since the crosslink density of H-NBR/SBR(3/7) blend was higher than that of NR/SBR(3/7) by a factor of 3. Consequently, the \( G \) of the NR/SBR blend was found to be dependent upon the strain-induced crystallization, which was concerned with not only morphology of the blend but also the crosslink density of NR.
4. Conclusions
The geometrical feature of the NR domain in the NR/SBR(3/7) blend was ellipsoidal rather than spherical and its average diameter was longer than about 1 μm, whereas the spherical domain of less than 1 μm in diameter was dispersed in the NR/SBR(1/9) blend. The $G$ of the NR/SBR(3/7) blend was divided into two curves after superposition: one for the $G$ measured at 273 K and the other at temperatures ranging from 298 to 333 K, though that of the NR/SBR(1/9) blend was superposed into the single master curve, as in the case of SBR. When the crosslink density of NR increased by a factor of 3, the abrupt increase in the $G$ for the NR/SBR(3/7) blend disappeared, suggesting that the increase in the crosslink density of NR suppresses the strain-induced crystallization. Thus, it is concluded that the strain-induced crystallization is controlled by not only the dimensional feature of the NR domain but also the crosslink density of NR.

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