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Proton Spin Lattice Relaxation in Blends of Natural Rubber and Polyterpene

Masayoshi ITO and Koji TANAKA
Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162

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Synopsis. NMR measurements were carried out on blends of natural rubber (NR) and polyterpene (PT). The blends of NR and PT are perfectly mixed. The motion of NR chains play a dominant role in the glass transition of the blends. The mobility of NR segments in the blends are constrained by the presence of PT.

Rubbery mixtures of an elastomer and resin are tack, and the tackiness increases with increase in the concentration of resin. Hock[1)] found by electron microscopy that the increase of tackiness is due to the development of a second phase, which probably consists of low molecular weight rubber dissolved in the resin. On the other hand, Fukuzawa[2)] suggested that the compatibility of elastomer-resin is the most important factor in understanding the increase of tackiness. These different explanations imply that detailed information on the internal structure of the blend materials is necessary to understand the increase of tack.

The application of NMR method to the study of polymer blends is known to offer advantageous information on the microstructure of the blend materials.[3,4)]

In the present study, the segmental mobility for the blends of natural rubber and polyterpene was investigated by the NMR method in order to further elucidate the mixing state of the blends.

Experimental

Samples. Unvulcanized natural rubber (Hevea rubber) and polyterpene which is a random copolymer of α-pinene and β-pinene (Sekisui Chemical Industry Co., Ltd.) were used. The number average molecular weight and softening point of polyterpene were 1200 and 100 °C, respectively. X-Ray diffraction patterns indicated that these materials are completely amorphous. The glass transition temperature of natural rubber and polyterpene was determined by DSC to be *ca.* −65 and 70 °C, respectively.

Films containing natural rubber and polyterpene were cast from carbon disulfide solution on glass at room temperature. The ratio of natural rubber to polyterpene is given on a weight basis. The films were dried in a vacuum at room temperature for a week.

Measurements. A pulsed NMR spectrometer similar to the one described by Clark[5)] was used. The resonance frequency for protons was 30 MHz. Samples were packed in a glass tube in a vacuum.

Line width was obtained with a JNM W-40 type (resonance frequency for protons was 40 MHz) broad line NMR spectrometer.

Results and Discussion

The temperature dependence of spin-lattice relaxation times (T_1) for natural rubber (NR), polyterpene (PT), and their blends is shown in Fig. 1. T_1 for NR and the four blends shows one T_1 minimum, indicating the presence of a second minimum below the temperature accessible in this study. In NR, the high temperature minimum undoubtedly corresponds to the glass transition, while the low temperature process involves methyl group reorientation.[6)] T_1 for PT shows one small minimum at around 150 °C, indicating the presence of two minima below and above the temperature accessible in this study. The low temperature process might be due to the methyl group reorientation as judged from

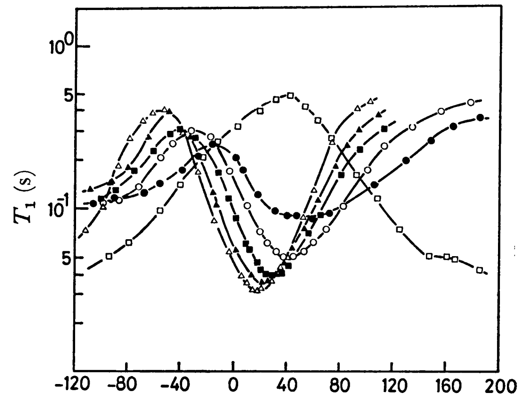

Fig. 1. Temperature dependence of T_1 for NR(△), PT(□), NR-PT=90: 10(▲), NR-PT=70: 30(■), NR-PT=50: 50(○), and NR-PT=30:70(●).

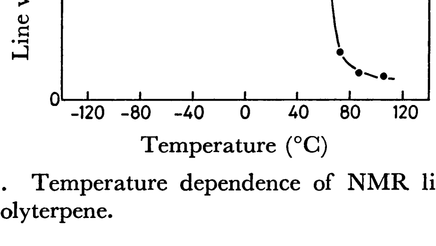

Fig. 2. Temperature dependence of NMR line width of polyterpene.

the very low T_1 minimum temperature and the chemical structure of polyterpene. The line widths for PT obtained from the derivatives of the broad line NMR absorption lines are plotted against temperature in Fig. 2. Two distinct transitions take place. At the first step the narrowing of line width starts at about 20 °C. After the first narrowing the curve enters into the second step of abrupt decrease at *ca.* 70 °C, followed by leveling off. The high temperature transition is consistent with the glass transition temperature of PT. A small decrease of line width at *ca.* 20 °C indicates a small scale segmental motion of PT. From a comparison of the line width data with the T_1 data (Fig. 1), it is postulated for the relaxation mechanisms of PT that the high temperature decrease of T_1 is due to the onset of micro-Brownian motions and the small T_1 minimum at around 150 °C corresponds to the local mode motions. On the basis of the characterization of T_1 minima for NR and PT, it is postulated for the relaxation mechanisms of the blends that the low temperature minimum is due to the reorientation of the methyl group and the high temperature process corresponds to the glass transition. As seen in Fig. 1, all the samples show only one T_1 value in the whole range of temperature. The fact that blends of natural rubber and polyterpene show only one glass transition and T_1 value over the whole range of composition and temperature demonstrates the excellent compatibility of NR and PT.

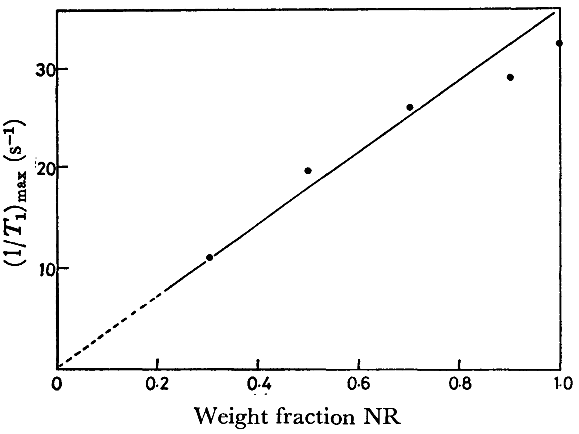

Fig. 3. Natural rubber weight fraction dependence of maximum relaxation rate at the glass transition.

Figure 3 shows the relation between the maximum relaxation rate $(1/T_1)_{\max}$ of the blends at the glass transition and the weight fraction of NR. A linear dependence is found. This indicates that the motion of the natural rubber chain plays a dominant role in the mechanisms of glass transition of the blends.

The T_1-temperature curve is gradually broadened at the glass transition and the minimum temperature shifts to the higher temperature side with the increase of PT content (Fig. 1). The broadening of the T_1 minimum indicates that the distribution of correlation times related to the degree of the restriction imposed on the segments is broadened by addition of the PT resin. With the increase of PT content, the intermolecular interaction between NR and PT chains increases and the segmental motion of NR in the blends is constrained and the temperature of the T_1 minimum shifts to the higher temperature side.

In conclusion, blends of natural rubber and polyterpene are perfectly mixed over the whole range of composition. The motion of the natural rubber chain plays a dominant role in the mechanisms of glass transition of the blends and the segmental mobility of natural rubber chains in the blends are greatly constrained by the presence of polyterpene.

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