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Dynamics of polybutadiene reinforced with unsaturated carboxylate studied by muon spin relaxation (μSR)

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ABSTRACT

Muon spin relaxation (μSR) measurements were performed to investigate the dynamics of polybutadiene (PB) reinforced by zinc diacrylate (ZDA). The spin relaxation rate was found to be almost independent of temperature below the glass transition temperature T_g, while it increased monotonically with temperature above T_g. In addition, the spin relaxation rate for PB including 14 vol% ZDA, which has a higher elastic modulus, was slower than that of PB without ZDA. Thus, μSR can clearly distinguish the dynamics of PB in these two samples, with the spin relaxations mainly caused by the so-called α-process (above T_g) and fast β-process (below T_g). To examine this scenario in detail, we performed μSR experiments as a function of longitudinal magnetic field (LF). The motional relaxation rate for PB was independent of temperature below T_g, confirming that the spin relaxation is mainly induced by the fast β-process. The α-process above T_g was also confirmed based on the Vogel–Fulcher-type temperature dependence, and the motional relaxation rate in the α-process was decreased by ZDA aggregates. These findings clearly show that μSR measurements provide useful information on the dynamics in complex polymer systems.

1. Introduction

For the last two decades, the dynamics of polybutadiene and other glass-forming materials have been extensively studied using various methods to reveal heterogeneous dynamics and the origin of the glass transition [1–5]. It is well known that glass-forming materials show sudden increases in elasticity or viscosity of more than 12 orders of magnitude without any discontinuous changes of structure in a very narrow temperature window (a few degrees) near the glass transition temperature T_g during cooling from supercooled liquid states. However, no definitive explanations have been presented for this drastic dynamic change at T_g without any discontinuous structural changes. Therefore, the glass transition continues to be a mystery.

From the viewpoint of industrial applications, polybutadiene is one of the most popular rubber materials and is used in automobile and airplane tires and base-isolating devices, which are indispensable in industry and daily life. Rubber materials that are applied to industrial products or devices are reinforced with the addition of fillers, such as carbon black, silica, and clay. Among the various available fillers, metal diacrylates, especially zinc diacrylate (ZDA), exhibit strong reinforcement properties [6]. To clarify the effects of ZDA on the reinforcement properties, we studied the hierarchical structure of polybutadiene reinforced by ZDA using small-angle neutron scattering (SANS) and small-angle X-ray scattering (SAXS) [6,7]. A highly crosslinked polybutadiene region was found to exist around ZDA aggregates, and this network with high-density regions produces high elasticity. As dynamics also greatly affect the properties of a material, knowledge of the dynamics of polybutadiene crosslinked by ZDA is also important for the industrial application of rubber materials. Owing to the hierarchical structure, the dynamics of rubber materials with fillers cover a wide range of time scales. Hence, the use of various experimental methods is necessary to reveal the whole picture of

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the dynamics. Therefore, in this paper, we conducted muon spin relaxation (μSR) experiments to study the dynamics of crosslinked polybutadiene and gain an understanding of the heterogeneous dynamics and the reinforcement effects of ZDA.

Muon-based experiments have been used in various research fields, although there are relatively few examples related to polymer dynamics [8–14]. Pioneering μSR work on the dynamics of neat polybutadiene was performed by Pratt et al. [11], in which a muon-induced radical state was used as a probe for the dynamical properties. They reported that the muon spin relaxation rate exhibited a significant change near the glass transition T_g, suggesting that μSR is useful for investigations of polymer dynamics. One of the aims of this work is to explore the possibility of using μSR experiments to probe the dynamics of polybutadiene reinforced with metal diacrylates, especially ZDA.

2. Experimental

2.1. Materials and sample preparation

The detailed composition of the samples used in the present study is summarized in Table 1. Polybutadiene (PB; BR730, JSR Co., Ltd., Tokyo, Japan) with a weight-average molecular weight M_w of 672000 and molecular weight distribution M_w/M_n of 2.39 was used, where M_n is a number-average molecular weight. The microstructure of PB was cis:trans:vinyl = 97:2:1. Zinc diacrylate (ZDA; Sanceler SR, Sanshin Chemical Industry Co., Ltd., Yanai, Yamaguchi, Japan) and dicumyl peroxide (DCP; Percmyl D, Nichiyu Co., Ltd., Tokyo, Japan) were used as the crosslinker and initiator, respectively, for the crosslinking reaction. The components were mixed for 5 min using a 6-inch two-roll mill, and molded into sheets about 1 mm thick at 170 °C for 20 min. The glass transition temperatures (T_g) of ZDA (0) and ZDA (14), where the vol% of ZDA in the sample is indicated in parentheses, obtained by differential scanning calorimetry (DSC) were 168.6 and 168.1 K, respectively. The elastic moduli of ZDA (0) and ZDA (14) at 293 K and 10 Hz obtained by dynamic viscoelasticity measurements were 4.0 and 104.6 MPa, respectively.

2.2. Measurements

Conventional μSR experiments were performed using the D1 instrument [15] installed at the muon facility (MUSE) in the Material and Life Science Experimental Facilities (MLF), J-PARC. Each sample was set on a sample holder made of silver and loaded into a helium gas-flow cryostat to control the temperature in the range between 30 and 280 K. For the μSR experiments under a longitudinal field (LF), an external magnetic field was applied parallel to the direction of the initial muon spin polarization over the rage of 10–2000 G. Muon decay positrons were detected by counters at forward and backward positions with respect to the initial muon spin polarization. The time-dependent asymmetry of the decay positrons was evaluated using the following equation:

$$f(t) = \frac{F(t) - \alpha B(t)}{F(t) + \alpha B(t)} \quad (1)$$

Table 1
Components of the samples used in the present study.

Sample	ZDA (0)	ZDA (14)
Polybutadiene (vol%)	99.5	85.2
Zinc diacrylate (vol%)	0	14.4
Dicumyl peroxide (vol%)	0.5	0.4

where $F(t)$ and $B(t)$ represent the number of positron counts in the forward and backward detectors, respectively, as a function of time, and α is the correction factor, which takes into account the relative efficiencies of the detectors [8]. To interpret the experimental results, it is important to obtain a reasonable estimation of the muon sites and local environment in the specimen. Muon is known to form muonium (analogous to a hydrogen atom, where the proton is substituted by a positive muon) in non-metallic materials [16–19]. Moreover, muonium can react with unsaturated bonds, such as C=C in the present samples. Many C=C bonds exist in the ZDA/PB system, with C=C bonds mainly from PB, as those in ZDA are likely exhausted following crosslinking during sample preparation [20]. Therefore, a significant fraction of muons in PB are considered to be located as muonium atoms (or muon-induced radicals), with spin relaxations dominated by fluctuations in the internal magnetic field exerted on them.

3. Results and discussion

The time-dependent asymmetry $f(t)$ in the LF-μSR experiments at LF = 100 G are shown in Fig. 1 for ZDA (0) and ZDA (14). Each spectrum was shifted vertically to see their differences. These spectra exhibit clear dependence on temperature, with clear differences between ZDA (0) and ZDA (14). To understand the results quantitatively, a sum of two stretched exponential functions (or Kohlrausch–Williams–Watts (KWW) functions) (Eq. (2)) was used to analyze the spectra using least-square curve fitting.

$$f(t) = A_1 \exp\left(-(1/\tau_1)^{\beta_1}\right) + A_2 \exp\left(-(1/\tau_2)^{\beta_2}\right) + B \quad (2)$$

where A_1 and A_2, τ_1 and τ_2, β_1 and β_2 are the amplitude of the partial asymmetry, relaxation time, and the exponent (reflecting the distribution of the spin relaxation time), respectively, for each component, and B is the non-depolarizing amplitude. The studied samples were very heterogeneous owing to the crosslinks and the filler ZDA [6,7], and hence a wide distribution of relaxation times is expected. We employed the stretched exponential function to evaluate the distribution of the spin relaxation times. In the curve fitting procedure, we found that β_1 was almost unity, indicating that the relevant component can be described by a single exponential function. Thus, we fixed $\beta_1 = 1$ in the fitting procedure. The results of the fits are shown by solid curves in Fig. 1a–b for ZDA (0) and ZDA (14), respectively, at various temperatures below and above T_g. As seen in Fig. 1, the data are well fitted, suggesting that the model function is acceptable for the analyses. From the fits, we found that the spin relaxation time τ_1 is about 1.0 μs and independent of temperature over the whole temperature range, whereas τ_2 exhibits strong temperature dependence, suggesting that the spin relaxation process for τ_2, which seems to be relatively slow, reflects the thermally activated motions of PB. The dependence of PB motion on temperature was also confirmed qualitatively by the temperature dependence of β_2. We therefore focus on this component hereafter to discuss PB molecular motions. An average spin relaxation time $\langle\tau_2\rangle$ for the slow process was calculated using Eq. (3) [21,22]:where Γ is a gamma function. The temperature dependence of the reciprocal average spin relaxation times $\langle\tau_2\rangle^{-1}$ is plotted in Fig. 2 for ZDA (0) and ZDA (14).

The reciprocal average spin relaxation time is almost temperature independent below T_g for both ZDA (0) and ZDA (14), and the values are almost identical for the two samples, suggesting that fluctuations of the magnetic fields at the muon site, presumably induced by PB motions, are minimal below T_g. It is well known that segmental motions and larger length-scale motions in polymers are suppressed in the glassy state. Therefore, the spin relaxation must