

# 9 Tribology Project

## – Photon and Quantum Basic Research Coordinated Development Program –

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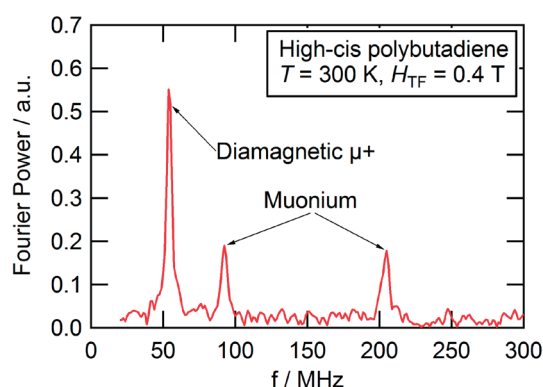
### 9-1 Introduction

Tribology is the science of interacting surfaces in relative motion, which includes the study and application of the principles of friction, lubrication and wear. It is closely related to our everyday life, from live cell friction to engine lubrication and seismology. It is estimated that the reduction of energy consumption by the optimization of friction and lubrication is worth 1.3 trillion yen in Japan, and thus it is important to understand the fundamental aspects of tribology. However, elemental processes can be seen at various spatial scales from angstrom to km, and the phenomena are essentially non-equilibrium. Additionally, tribological phenomena occur at buried interfaces. Thus there are many unsolved problems, both theoretical and experimental.

In this project, we intend to utilize neutrons and muons to investigate friction and lubrication, because these probes are powerful tools for in-situ investigation of buried interfaces, and also complementary methods to observe the dynamical behavior of molecules and molecular assemblies.

### 9-2 Dynamical behavior of polymer molecules probed by muon spin relaxation

Energy dissipation in rubber materials is closely related to the local dynamics of atoms/molecules of polymer chains. When stress is applied to a rubber, a part of the energy is stored as elastic energy and the rest may dissipate through a variety of channels including local atomic and/or molecular motions which cause energy loss. Controlling this kind of energy loss is one of the key issues in the development of rubbers for low-fuel

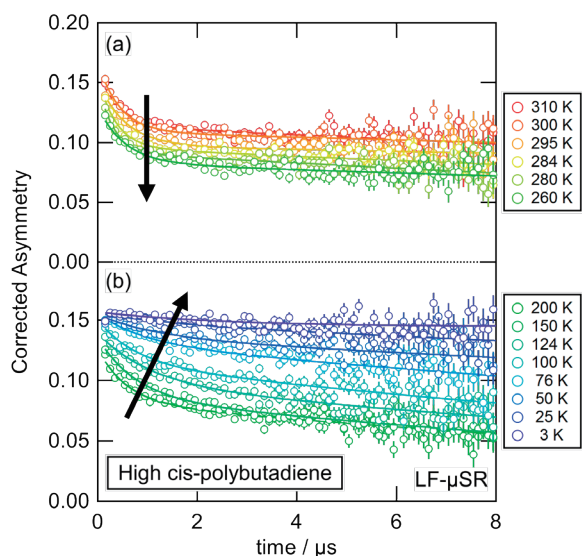


**Fig. 1:** Fast Fourier Transformation of a  $\mu$ SR time spectrum at 300 K under TF = 400 mT.

consumption tires.

Considering that the characteristic time scale (frequency) of polymer dynamics may spread from  $10^0$  to  $10^{12}$  Hz, it is important to obtain information on the dynamics of polymers by combining various experimental techniques having different time windows, such as neutron scattering, acoustic sound attenuation, dielectric relaxation and viscosity measurement. There is a gap in the characteristic time range of these conventional experimental techniques, which can be covered by muon spin rotation/relaxation ( $\mu$ SR). This means that  $\mu$ SR can provide complementary information through the channel of spin fluctuation.

The objective of this project is to clarify the dynamical behavior of polymer molecules over the specific frequency region mentioned above, where the characteristic time scale presumably corresponds to the local atomic or molecular motions. To this end, we chose polybutadiene (PBD) rubber as the prototype polymer system, and performed  $\mu$ SR measurements for high cis-PBD rubber. The local electronic state of muon [muonium (Mu) or diamagnetic muon] was identified by



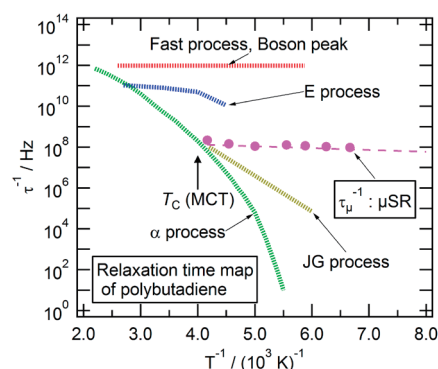
**Fig. 2:**  $\mu$ SR Time spectra under longitudinal magnetic field (LF = 20 mT) at the temperature range of (a)  $310\text{ K} > T > T_{cr} = 254\text{ K}$  and (b)  $T_{cr} > T > 3\text{ K}$ .

measurements under a transverse magnetic field (TF), and the fluctuation rate of the hyperfine field was deduced from them under longitudinal fields (LF). It is inferred from the fast Fourier transformation (FFT) of TF- $\mu$ SR time spectra (Fig. 1) that the signal consists of diamagnetic muon and Mu component. The LF- $\mu$ SR time spectra under LF = 20 mT exhibit a weak enhancement of depolarization and asymmetry shift with decreasing temperature above the crystallization temperature  $T_{cr} = 254\text{ K}$  [Fig. 2(a)], and strong suppression of depolarization below  $T_{cr}$  [Fig. 2(b)].

In order to obtain fluctuation frequency  $\nu$  of the hyperfine field that may be linked with the local molecular motion around the muonium, we have analyzed the obtained time spectra under LF = 20 mT using the following depolarization function, where  $G_{dMu}$  is a dynamical muonium

$$A(t) = A_1 \exp(-\lambda_1 t) + A_2 G_{dMu}(B, A_{hf}, \Delta, \nu, t) + A_3, \quad (1)$$

depolarization function,  $B$  is a longitudinal magnetic field,  $A_{hf}$  is a hyperfine parameter between muonium and electron, is magnetic field distribution width due to proton nuclear spin, and  $\nu = 1/\tau$  is fluctuation frequency of the proton. The obtained fluctuation frequency ( $\tau_{\mu}^{-1}$ ) as a function of reciprocal temperature is shown in Fig. 3. The frequency  $\tau_{\mu}^{-1}$  shows least coincidence with  $\alpha$  or Johari–Goldstein (JG) relaxation processes, but merges with these well-known relaxation processes at around  $T_c \sim 250\text{ K}$  (Fig. 3 filled circles). This may suggest a relaxation process of hitherto unknown origin in polybutadiene. However,



**Fig. 3:** Relaxation time map of polybutadiene. Filled circles are obtained from  $\mu$ SR and other lines are referenced from the report [1].

there is a certain ambiguity that the high cis-polybutadiene has two coexisting phases below  $T_{cr}$ , where only one of these corresponding to the amorphous region shows a glass transition at 168 K. Detailed research is in progress to examine whether the observed behavior is related to the crystallization.

In summary, we have performed  $\mu$ SR measurement of the high cis-PBD under TF and LF. The time spectra indicate the presence of diamagnetic muon and muonium components. From the analysis of the LF- $\mu$ SR time spectra, it was found that the temperature dependence of fluctuation frequency for the hyperfine field does not coincide with well-known  $\alpha$  and JG relaxation processes, suggesting a relaxation of hitherto unknown origin. Despite ambiguity as to the relation between the observed relaxation and crystallization, we conclude that  $\mu$ SR can be used to probe the dynamics of polymers around the MHz band.

### 9-3 Aggregation structure and thermal molecular motion of elastomer at an inorganic material substrate

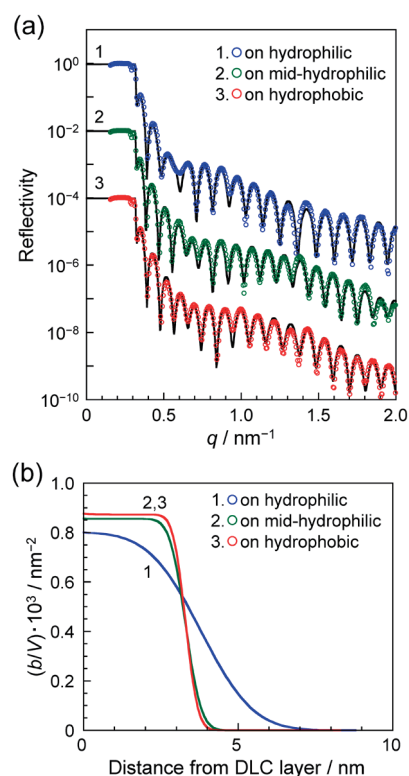
The interface between polymers and inorganic materials is of pivotal importance both technologically and scientifically. An example is a nanocomposite, which is a class of materials composed of polymers and inorganic fillers. In general, the performance of a nanocomposite strongly relies upon the interfacial structure and physical properties of the composite. This means that an understanding of interfaces is essential in order to construct highly functionalized materials. The same is true for tire materials; because the main components of tire materials are elastomer and carbon fillers, an understanding of the interface between

elastomer and carbon fillers should be important.

A nanometer-thick layer, the so-called bound rubber layer (BRL), is typically formed on the carbon filler surfaces and is resistant to dissolution, even in a good solvent which interacts favorably with the polymer. In theory, the interactions between polymers and carbon filler surfaces restrict molecular motion, which correlates with increased resistance to mechanical deformation as compared to free polymers which are located away from the carbon filler surface. However, the aggregation structure and thermal molecular motion of elastomer molecules in BRL are still unknown. Furthermore, it is also still unknown how the chemical composition of the carbon surface affects the structure and motion of elastomer molecules although functional groups at the filler surface strongly affect the performance of tires [2]. The purpose of this study is to investigate the relationship between the wettability of a carbon surface and aggregation structure, as well as the thermal molecular motion of BRL.

For this purpose, a model system of the interface, namely PBD thin film on a diamond-like carbon (DLC) layer, was prepared. To extract BRL, the films were rinsed by *p*-xylene and well dried at room temperature prior to the measurement. Fig. 4(a) shows the X-ray reflectivity (XR) profile for a BRL on DLC film. In Fig. 4(b), open symbols denote experimental data, and solid curves are calculated reflectivity based on model scattering length density ( $b/V$ ) profiles. For clarity, each data set for the BRL is offset by two decades. Since the calculated reflectivities are in good agreement with the experimental data, it can be considered that the model ( $b/V$ ) profiles well reflect the density profiles of the bilayer along the direction normal to the surface. Although film thicknesses of the BRLs were independent of the wettability of the DLC films, ( $b/V$ ) values corresponding to the density of BRLs were not independent. The density of BRL on hydrophobic DLC is the largest and that on hydrophilic DLC is the smallest, which could be reasonable considering that PBD is a hydrophobic component. Note that the density of BRL on hydrophobic DLC is comparable to that of bulk in the glassy state. Thus, it is expected that the molecular motion of the PBD chains in BRL depends on the wettability of DLC because of the density difference.

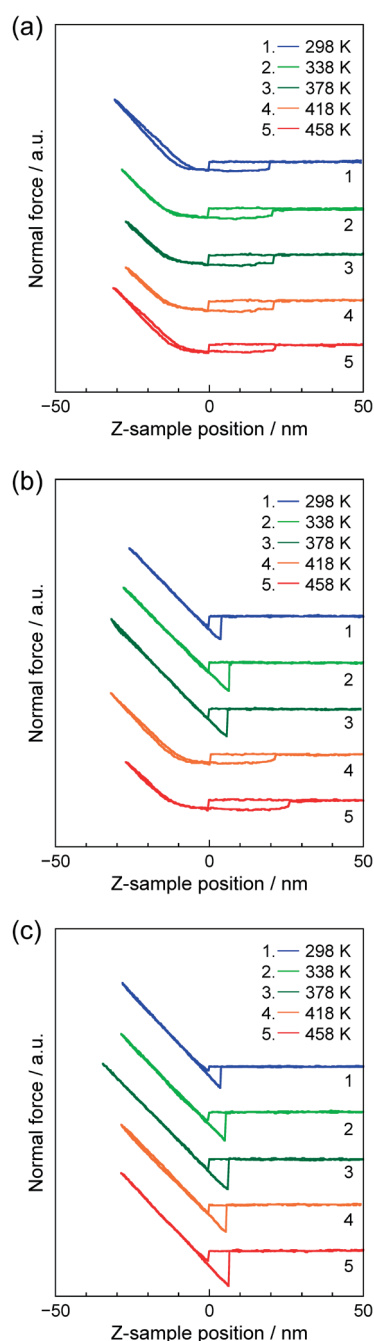
To understand the relationship between thermal molecular motion of the polymeric chains in



**Fig. 4:** (a) X-ray reflectivity curves for BRL on DLC layers. Open symbols denote experimental data. Solid curves are calculated reflectivities on the basis of model scattering length density ( $b/V$ ) profiles shown in panel (b).

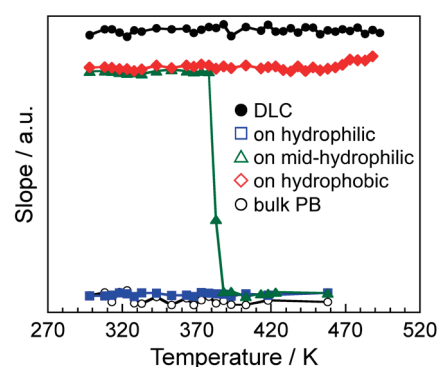
BRL and those of the aggregation structure, force-distance curves were measured. When the cantilever tip contacts with a specimen in the approach direction, the normal force drops because of van der Waals force between them. If Young's modulus of the specimen is in the order of GPa, namely the BRL is a glassy state, the normal force immediately increases as the vertical position decreases. On the other hand, when Young's modulus of the specimen is much smaller than a few GPa, which means that the BRL is in a rubbery state, the normal force does not increase because of the deflection of the BRL. However, when the film thickness of the BRL is less than 10 nm as shown in Fig. 4(b), the normal force increases even if the BRL is in the rubbery state and the vertical position is less than  $-10$  nm.

Fig. 5 shows the force-distance curves of BRLs at various temperatures. In the case of the BRL on hydrophilic DLC, the slope in the vicinity of the sample surface was almost zero even at 298 K as shown in Fig. 5(a). After elevating the temperature, the shapes of the force-distance curves were almost the same. This result implies that the BRL on hydrophilic DLC is already



**Fig. 5:** Temperature dependence of force-distance curves for BRL on (a) hydrophilic, (b) mid-hydrophilic and (c) hydrophobic DLC layers.

rubbery at 298 K. In case of the BRLs on mid-hydrophilic and hydrophobic DLC, the normal forces immediately increased as the vertical position decreased at 298 K as shown in Fig. 5(b) and (c). This clearly indicates that the thermal molecular motion of the PBD chains in the BRLs on mid-hydrophilic DLC and hydrophobic DLC is different from that in the BRL on hydrophilic DLC. The tendency lasted until 378 K for the BRL on mid-hydrophilic DLC and did not change until at least 458 K for the BRL on hydrophobic DLC, respectively. At 418 K for the BRL on mid-hydrophilic DLC, the



**Fig. 6:** Correlation between temperature and slopes obtained from the result of force-distance curves for BRL on DLC layers.

slope in the vicinity of the surface became almost zero. Thus, the transition from glassy state to rubbery state, namely, the apparent glass transition temperature ( $T_g$ ) of the BRLs on mid-hydrophilic and hydrophobic DLC, occurs at a much higher temperature than that of the BRL on hydrophilic DLC.

The values of the slopes were extracted from all the force-distance curves. Fig. 6 shows the relationship between the slope and measurement temperature. For comparison, the slopes extracted from DLC film and bulk PBD are also shown in the figure. In the case of bulk PBD, the slope was almost zero above 298 K since  $T_g$  evaluated by differential scanning calorimetry was 173 K, which is much lower than 298 K. The same tendency was observed in the case of the BRL on hydrophilic DLC. On the other hand, the BRLs on mid-hydrophilic and hydrophobic DLC had certain values at 298 K and dropped at approximately 320 K and 380 K for the BRLs on mid-hydrophilic and hydrophobic DLC, respectively. This indicates that the wettability of the DLC film strongly affects not only the density of the BRL but also the thermal molecular motion of PBD chains in BRL.

### Acknowledgement

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### References

- [1] Kanaya et al., *J. Phys. Soc. Jpn.* **74** (2005) 3236.
- [2] Nomura et al., *Polym J*, **15** (1983) 201.