6 Tribology Project

Photon and Quantum Basic Research Coordinated Development Program –

6-1 Introduction

Tribology is the science of interacting surfaces in relative motion including the study and application of the principles of friction, lubrication and wear. It is closely related to our everyday life, in diverse areas from live cell friction to mechanical parts 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 both the industrial applications and fundamental science of tribology. Elemental processes of phenomena can occur at various spatial scales from angstrom to km, and the phenomena are essentially non-equilibrium. Additionally, the phenomena occur at buried interfaces and are difficult to observe in situ. For these reasons, fundamental aspects remain unsolved at both the theoretical and experimental level.

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 are complementary methods to observe the dynamical behavior of molecules and molecular assemblies.

6-2 Development of magnetic marker µSR method for probing molecular dynamics

Energy dissipation in rubber materials is closely related to the dynamics of constituent molecules. When stress is applied to a rubber, some energy is stored as elastic energy and the remainder dissipate through the channels of atomic and/ or molecular motion which causes energy loss. Controlling this kind of energy loss is one of the

Project Leader: Hideki Seto

key issues in the development of rubbers such as low-fuel consumption tires.

According to the thermal-dissipation theorem, the response received from the outside is the same as the response to spontaneous fluctuation such as molecular dynamics. In regard to the dissipating energy, the energy propagates through various molecular dynamics modes and is finally converted to thermal energy. If such significant dynamics modes are elucidated by microscopic methods, it is expected that this will accelerate the development of elastomer such as high-performance rubber.

Considering that the characteristic time scale (frequency) of molecular dynamics may extend from 10^o to 10¹² Hz, it is important to obtain information on the atomic/molecular processes using a combination of various experimental techniques



Fig. 1: (a) Frequency dependence of loss tangent $\tan(\delta)$ in typical tire materials. The $\tan(\delta)$ at 10^1 Hz must be low a tire with good fuel consumption, while $\tan(\delta)$ at 10^6 Hz must be high for a tire with good grip. (b) The characteristic time window of several microscopic methods. μ SR can cover the gap between nuclear magnetic resonance (NMR) and quasi elastic neutron scattering (QENS).



Fig. 2: μ SR time spectra in PBD under several weak LF collected at 250 K, 200K, and 90K. The 90K spectra changes with the application of LF indicating the existence of a static component, while the 250 K spectra does not exhibit such variation due to LF indicating no static component.

with different temporal windows, such as neutron scattering, acoustic sound attenuation, and viscosity measurement. However, there is a gap in the characteristic time range of those popular experimental techniques, which can be addressed by muon spin rotation/relaxation (μ SR, Fig. 1). This suggest that μ SR can provide complementary information via the channel of spin fluctuation. However, there are only a few reports on the dynamics of polymers using μ SR [1, 2].

We have performed µSR measurement for polybutadiene (PBD, one of the pristine materials used for rubber products) to address polymer dynamics. The results of this measurement under weak longitudinal magnetic fields (LF) indicate that both dynamical and static components exist even below the glass transition temperature (Fig. 2). From data analysis, we have obtained the fluctuation rate of dynamical components as shown



Fig. 3: Relaxation time map of PBD. Filled circles are obtained from μ SR and the other lines are references from the report [3].

in Fig. 3. By comparing this result with the fluctuation mode observed by other methods such as neutron scattering and dielectric relaxation, it was determined that the observed dynamics obtained using μ SR differs from the fluctuation obtained using the other techniques. In the process, we identified a novel molecular dynamics mode in the MHz region, had not been discovered using other techniques. The new finding is partially attributable to the fact that only μ SR can probe MHz dynamics.

To obtain spatial information of the observed dynamics, we focused on the hyperfine field from proton spin. Assuming a chemical structure model, we calculated the hyperfine field using Van-Vleck summation. For the case of a polycrystal-line sample under zero magnetic field (ZF), Δ can be calculated using the following equation,

$$\Delta_{VV,ZF}^{2} = \frac{1}{3} \gamma_{\mu}^{2} \gamma_{I}^{2} I(I+1) \hbar^{2} \Sigma_{i} r_{i}^{-6}, \left(I = \frac{1}{2}\right),$$

where *I* is the nuclear spin, \hbar is Plank's constant, *r* is the distance between a muon and proton, and γ_{μ} , γ_{I} are the gyromagnetic ratio of muon and nuclear spins, respectively. From data analysis, we obtained the value of the hyperfine field, $\Delta_{obs} = 0.62 \pm 0.13$ MHz. In order to explain the observed value, we had to consider the contribution from protons of a neighbouring chain. This fact indicates that muon in PBD probe interchain dynamics (Fig. 4).



Fig. 4: One microscopic model of molecular dynamics observed using μ SR. At a minimum, we must consider the contribution from not only intra-chain protons, but also inter-chain protons to explain the obtained results.

6-3 Structural properties of elastomer thin films bound to model filler interfaces

The interfaces between polymers and inorganic materials are of pivotal academic and industrial interest. An example of this is the interface in nanocomposites, a class of materials composed of polymers (matrix) and inorganic nanoscale powders (fillers). In general, the performance of a nanocomposite strongly depends not only on the physical properties of the matrix but also on the interaction between the matrix and the filler material. It is noteworthy that the physical response of a composite can be modulated via the interactions resulting from the attachment/detachment of polymers to the fillers. This means that an understanding of the interfaces between the polymer matrix and inorganic fillers is essential to construct highly functionalized nanocomposites.

A specific example is tire materials; because the rubber used for tires consists mainly of a polymer elastomer matrix and carbon/silica fillers, an understanding of the interface between the polymer and the filler is important for improving quality. In the case of a carbon filler, a nanometerthick layer called the bound rubber layer (BRL), is typically formed on the carbon surface and is resistant to be dissolved even in a good solvent. In theory, the interactions between polymers and carbon material surfaces restrict molecular motion, which correlates with increased resistance to mechanical deformation compared to free polymers that are located away from carbon material surfaces. On the other hand, since the affinity between silica and polymers is poor, a coupling

agent (CA) is used to reinforce the resistance of BRL in the case of a silica filler. In this scenario, the structure and physical properties of the BRL can be controlled by changing the kind of CA, namely, the chemical properties of the filler surface.

Significant effort has been made in industry to manufacture high-performance tires using surface-modified fillers. Since the structure and/or thermal molecular motion of polymers at the filler/ polymer interface is affected by the interactions with the fillers, it is believed that surface modification changes the properties of the BRL, resulting in an improvement in the tire's performance. However, this is still hypothetical, because there is insufficient evidence and empirical data, e.g., on the influence of surface modification on the BRL. The relationship between the BRL and tire performance needs to be evaluated to develop guiding principles for improving tire performance. Although the number of reports on the general BRL framework is increasing, it is still unclear how the surface modification of fillers affects the structural and mechanical properties of BRLs. [4]

In this study, we have investigated the distribution of styrene-butadiene rubber (SBR) on silica surface using neutron reflectometry (NR) and observed the selective distribution of the styrene functional group near the surface. Based on this knowledge, we investigated the distribution change of the styrene functional group depending on the kind of coupling agent.

Figure 5 (a) shows the NR curves of a SBR thin layer on a silica substrate treated with Si266 (bis[3-(trimethoxysilyl)propyl]disulfide), Si363



Fig. 5: (a) Neutron reflectivity curves of SBRs on silica substrate treated with SAM, Si266, and Si363. (b) The scattering length density distributions obtained from the model fittings.

(bis[3-(triethoxysilyl)tridecyl]disulfide) and SAM (propyltrimethoxysilane). In these samples, the butadiene groups are deuterated in order to observe the heterogeneous distribution of the styrene groups and the butadiene groups. Since the model fittings shown by the solid lines well reproduced the experimental data, this indicates that the model scattering length density (SLD) shown in Fig. 5 (b) seems to be a plausible profile. The SLD of the SBR on the SAM-treated silica is constant, however, the SLD's on the Si266- and Si363-treated silica surfaces are larger than those of the bulk SBR near the silica surface. These results suggest that the density of the SBR increases and/or the segregation of the butadiene groups occurs near the surface. The former possibility has been eliminated using X-ray reflectivity measurements. Thus, it is concluded that the segregation of the butadiene groups is induced by the effect of the coupling agents.

Reference

- [1] R. Mashita et al., Polymer **105** (2016) 510.
- [2] F.L. Pratt et al., Polymer **105** (2016) 516.
- [3] T. Kanaya et al., J. Phys. Soc. Jpn. 74 (2005) 3236.
- [4] K. Hori et al., Langmuir **33** (2017) 8883.

Acknowledgement

The reported experiment was partially supported by the Photon and Quantum Basic Research Coordinated Development Program by MEXT.