Quasielastic Neutron Scattering Study on Polymer Nanocomposites

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Abstract. By using a quasielastic neutron scattering technique (disk-chopper-type spectrometer AMATERAS at J-PARC), we have investigated the microscopic dynamics of polybutadiene (PB) in which silica particles were embedded. The experimental results gave us both a damped vibration mode of PB and jumped diffusion motion of the segments. It was found that these dynamical features remain unaffected by the presence of the silica particle, while the residence time of the jumped diffusion motion becomes longer at the high filler loading.

1. Introduction

It is well known that the incorporation of nanofillers to a polymer improves its mechanical property. Thus, polymer nanocomposite have been widely used in the industrial field. Numerous experiments have been attemped to elucidate how the nanofillers improve the mechanical property. However, most previous studies focused on the macroscopic nature including rheological, calorimetric and dielectric characteristics. Thus, it is still unclear how such macroscopic nature relates to the microscopic nature of a polymer. In recent years, by employing a neutron spin echo technique that is a powerful tool to observe polymer dynamics directly, several experimental results to reveal the relation between a microscopic and a macroscopic view on the relaxation dynamics of polymer in the presence of fillers. It is reported that the increase in the filler concentration does not affect the basic segmental relaxation rate (Rouse rate) but decreases the diameter of tube (the reputation tube) [1].

A quasielastic neutron scattering (QENS) technique allows one to observe the dynamics of polymer chains directly with a time scale of $\sim 10^{-12}$ s, and numerous studies have been studied on pure polymers. Kanaya and co-workers showed a damped vibration mode and local conformation transition of polybutadiene (PB) using QENS [2]. Although some QENS studies on polymer nanocomposites were also reported [3], the question of how the microscopic dynamics is affected by the presence of fillers remains unrevealed. To answer the question we used silica nanofillers embedded in a PB matrix as a model and aimed to clarify the effect of the fillers on the dynamics of polybutadiene by means of QENS.

2. Materials and Methods

2.1. Sample Preparation

Two kinds of silica (Si)-polybutadiene (PB) nanocomposites were used for this study. The sample characteristics are tabulated in Table.1. The PB used in this study was UBE UBEPOL BR150B(Ube Industries. Ltd.). Microstructure, molecular weight and distribution of polybutadiene is cis: trans: vinyl = 98: 1: 1 (wt.%), $M_w = 5.0 \times 10^5$ and $M_w/M_n = 2.8$, respectively. Si pellets (Ultrasil VN3, Evonik) and a silane coupling agent (Si266, Degussa GmbH) were used. These samples were mixed with an internal mixer and then laminated to be 2.0 mm thickness with two roll mills. To avoid multiple scattering, these samples were further sliced to be 0.4 mm thickness for QENS experiments.

Table 1. Compositions of the samples used in this study (phr[a])

Sample	VF(%)[b]	PB	Silica	Si266[c]	ZnO	Stearic acid	Sulfur	Acc. CBS[d]	DPG
Φ_{15}	14.5	100	40	3.2	2.5	2.0	1.5	1.7	2.0
Φ_{24}	23.8	100	75	3.2	2.5	2.0	1.5	1.7	2.0

[a] Parts per one hundred rubber by weight. [b] volume fraction of silica. [c] Bis-triethozysilylpropyldisulfane.
[d] N-cyclohexyl-2-benzothiazole sulfenamide.

2.2. Quasi-Elastic Neutron Scattering (QENS)

QENS experiments were performed at a cold neutron disk-chopper-type spectrometer (AMATERAS, BL14) installed at Material and Life Science Experimental Facility (MLF) of J-PARC [4]. The energy resolution is about 0.12 meV. The experimental temperatures used were 1, 27, 47, and 88 ºC.

2.3. Data Analysis

Dynamic structure factors $S(Q,\omega)$ obtained from the QENS experiments were first fitted with a model scattering function given by the sum of a δ-funcion and Lorentzian function. However, we turned out that the agreement between observed and calculated spectra was not so good. Therefore, we instead fitted the observed spectra with a funcion given by the sum of a δ-funcion and two Lorentzian functions expressed by the following equation:

$$S_{inc}(Q,\omega) = C(Q,\,\omega)\{A_\delta\delta(\omega) + A_n(Q)L(Q,\,\omega,\,\Gamma_n) + A_b(Q)L(Q,\,\omega,\,\Gamma_b)\} + B_{in}(Q)\,, (1)$$

where $C(Q,\omega)$ is a dynamic structure factor of the Si filled PB at T=-223 ºC, $\delta(\omega)$ is a δ-function, $L(Q,\omega,\Gamma)$ is a Lorentz function, $B_{in}(Q)$ is an inelastic background, A_n and Γ_n are prefactor and half width at half maximum (HWHM) of the narrower Lorentz function, and A_b and Γ_b are a prefactor and HWHM of the broader Lorentz function, respectively. The fitting was performed with the DAVE Peak Analysis (PAN) software developed by National Institute of Standard Technology(NIST) [5].

The mean-square displacement $\langle U^2 \rangle$ was evaluated through equation $I_{el}(Q) = \exp[-\langle U^2 \rangle Q^2]$ where $I_{el}(Q)$ is elastic scattering intensity.

3. Result and Disucussion

Figure 1 shows the dynamic structure factor $S(Q,\omega)$ of the sample Φ_{24} at 47 ºC and $Q = 2.09$ Å^{-1}. The thick solid line calculated $S(Q,\omega)$ from equation (1). is in a good agreement with the experimental data.

Figure 2 shows the Q dependence of HWHM of the broader Lorentz component Γ_b at 47 ºC. Γ_b is almost independent of Q. Thus, it is reasonable to suppose that the observed dynamics is a localized
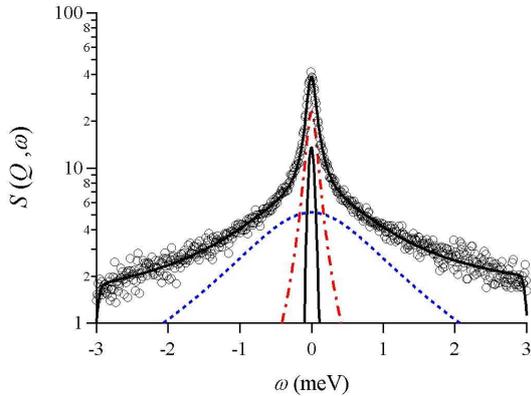
Figure 1. Quasielastic neutron-scattering spectra of sample Φ_{24} at Q=2.09 Å^{-1} and 47 ºC. Thick solid line indicates fit result according to equation (1). Dotted line, dash-dot line and thin solid line indicate broader Lorentz, narrower Lorentz and δ-funcion.
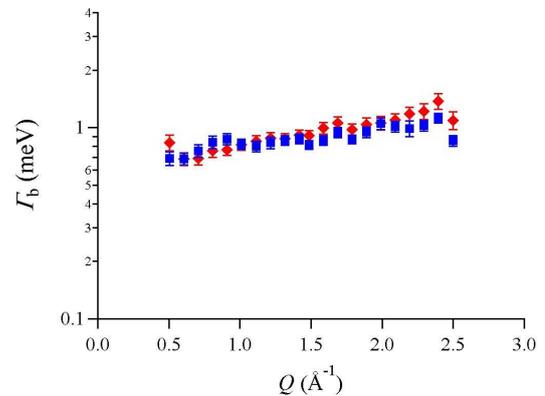

Figure 2. Q dependence of HWHM Γ_b of sample Φ_{24} at 47 ºC.($\blacklozenge$) : Φ_{15}, ($\blacksquare$) : Φ_{24}.

motion. The characteristic time τ derived from the relation of $\tau = h/\Gamma_b$ is estimated to be 5.5×10^{-12} s, where h is the plank constant.

Figure 3 shows the temperature denpendence of Γ_b at $Q = 2.09$ Å^{-1} plotted in the arrehenius fashion. The red and blue circles denote the Γ_b values for sample Φ_{15} and Φ_{24}, respectively. Both Γ_b values show a weak temperature denpendence and the estimated activation energy are 0.91 kcal/mol for sample Φ_{15} and 0.87 kcal/mol for Φ_{24}, respectively.

A QENS study on pure PB was reported by Kanaya and co-workers [2]. They showed a localized motion with an activation energy of about 0.5 kcal/mol. This motion was assinged to a damped vibrational motion of PB because the characteristic times of the motion was about 5.0×10^{-12} s at 45 ºC, which is too fast for the conformational transition. The time range and activation energy of the observed motion in this study are the same order of those of the pure PB reported. Thus, the observed motion corresponds to the damped vibraional motion of the PB in the presence of the Si fillers.

Figure 4 shows the Q^2 dependence of HWHM of the narrow Lorentz function Γ_n at 47 ºC. In the low Q region, Γ_n is proportional to Q^2 and becomes plateu at the high Q region. These characteristic Q-dependent features can be modeled as a jumped diffusion motion[6] expressed by equation (2):

$$\Gamma = h\frac{DQ^2 + (1 - \exp(-\langle U^2 \rangle Q^2))/\tau_0}{1 + DQ^2\tau_0} \tag{2}$$

where τ_0, D and $<U^2>$ are a residence time, diffusion coefficient, and mean square displacement, respectively. In the low Q region, equation (2) becomes simple diffusion:

$$\Gamma = hDQ^2 \tag{3}$$

On the other hand, in the high Q region, equation (2) becomes a constant value:

$$\Gamma = \frac{h}{\tau_0} \tag{4}$$

The solid lines in Figure 4 represent the best fits of equation (2) to the experimental data. In this study, the energy resolution was about 0.12 meV so that it is difficult to estimate a diffusion constant D from the low Q region of $Q < 1.0$ Å^{-1}. Instead, we used the high Q region to obtain the residence

time τ_0. The residence time τ_0 for the samples Φ_{15} and Φ_{24} are estimated to be 35.3 ps and 50.8 ps, respectively.

It was reported that pure PB shows a jumped diffusion motion with its residence time τ_0 of 81 ps and 48.6 ps for 23 ºC and 60 ºC, respectively [2]. By interpolating these reported data, the residence time τ_0 at 47 ºC is estimated to be about 58 ps. Hence, it is obvious that the residence time of the Si filled PB is shorter than that of pure PB. This may be due to the molecular weight or microstructure
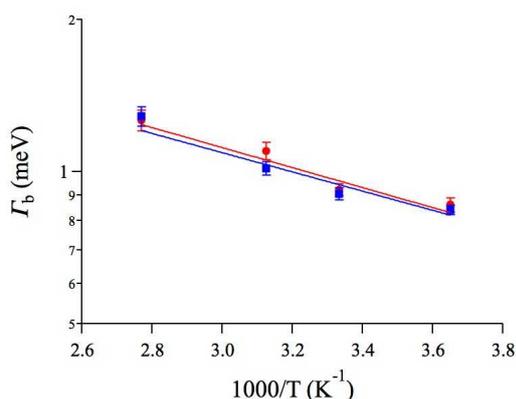

Figure 3. Temperature dependences of HWHM of the broad quasielastic components Γ_b at $Q = 2.09$ Å^{-1}. ($\blacklozenge$) : Φ_{15}, ($\blacksquare$) : Φ_{24}.
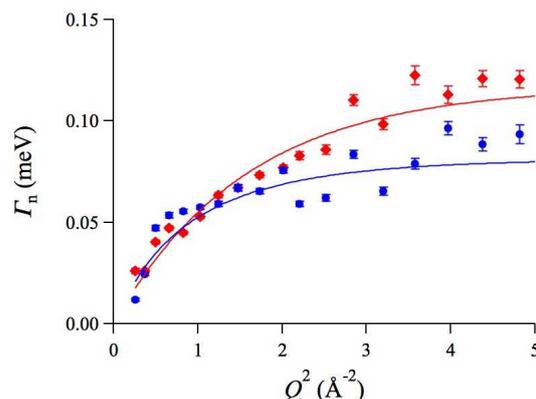
Figure 4. Q^2 dependences of HWHM of narrow quasielastic components Γ_n at 47 ºC. ($\blacklozenge$) : Φ_{15}, ($\blacksquare$) : Φ_{24}.

difference in PB used in this study. Further studies are currently in progress to see the effects of the addition of Si particles to the PB. The important finding in this study is that the increase in the Si concentration makes the residence time τ_0 longer.

If we assume all the Si particles are well dispersed in the polymer matrix, the distances between the nearest neighbor Si particles are estimated to be 29.7 nm for samples Φ_{15} and 25.2 nm for Φ_{24}, respectively, based on the volume fraction of the Si and its mean diameter (= 17.2 nm). Given the fact that the radius of polymer gyration (R_g) of the PB is 12.9 nm, the polymer chains are confined between the Si particles and squeezed to be 48 % for the sample Φ_{15} and 31 % for the sample Φ_{24}, respectively. We postulate these confinement effects make the local conformation transition of the polymer slow down, resulting in the longer residence time τ_0 at the higher Si loading.

4. Conclusion

The QENS experiments allowed us to investigate the in-situ microscopic dynamics of PB filled with the Si fillers. We found that the increase in the Si concentration makes the residence time τ_0 longer.

5. Acknowledgment

6. References

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