



Effect of silica nanoparticle filler on microscopic polymer α -relaxation dynamics

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Abstract Tyre rubber has been continuously developed to improve its performance, but the microscopic mechanisms behind these improvements, e.g. by adding nanoparticles to the rubber, are still not fully understood. We study the microscopic polymer dynamics of a rubber nanocomposite system consisting of polymer polybutadiene with 20 volume% of silica nanoparticles with diameters of 100 nm via quasi-elastic scattering experiments using gamma-ray time-domain interferometry. The result shows that the presence of silica nanoparticles caused the inter-chain α -relaxation dynamics to slow down in a shallowly supercooled state suggesting that the presence of the nanoparticles that came in contact with the polymer controlled the timescale of the polymer's α -relaxation dynamics. Conversely, the presence of nanoparticles less affects the dynamics in a lower temperature region near T_g . It is consistent with the result of the differential scanning calorimetry study showing negligible T_g difference among the pure polymer and the nanocomposite system. It also shows that the quasi-elastic scattering experiment can be used to reveal the polymer dynamics in nanocomposites and is appropriate for characterising their microscopic dynamics for the purpose of improving tyre performance.

Keywords Rubber · Nanocomposite · Quasi-elastic scattering · Time-domain interferometry

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1 Introduction

Tyre rubber has been continuously developed to improve various aspects of its performance, such as its grip performance, fuel efficiency and wear resistance, by adding fillers and cross-linking agents to the rubber [1, 2]. However, the microscopic mechanisms behind these improvements are still not fully understood, and gaining a better understanding of them will be highly important if we are to further improve tyre products. Static and dynamic studies using quantum beams, such as X-rays and neutron probes, as well as simulation studies have been undertaken for this purpose. The heterogeneous and hierarchical structure of fillers (nanoparticles) in rubber nanocomposite systems has been studied using electron microscopy and small-angle X-ray scattering (SAXS) measurements, and their nanoparticle and polymer dynamics have been studied across a wide range of spatial scales by quasi-elastic scattering methods. Such scattering methods are widely used to study complex nanocomposite systems because they enable us to determine the spatial and temporal scale of the dynamics. Microscopic polymer dynamics have been studied by quasi-elastic neutron scattering and neutron spin echo methods [3–11], and filler dynamics have been measured using X-ray photon correlation spectroscopy [12]. These studies have shown that there are immobile polymer shells around the nanoparticles and that these affect the rubber's macroscopic properties. Molecular-scale dynamics studies have revealed that the presence of nanoparticles slows down the microscopic segmental α -relaxation motion and increases its heterogeneity [7, 8]. However, we still do not have a complete picture of the microscopic dynamics, e.g. the microscopic behaviour of the polymer α -relaxation in deeply supercooled states.

Quasi-elastic gamma-ray scattering (QGS) using multi-line time-domain interferometry can be used to measure microscopic dynamics at particular timescales in the nanosecond to microsecond range [13–15]. Both the diffusive α -process and the local Johari–Goldstein process of polymers can be studied at these timescales [16]. To investigate the effect of nanoparticles on the microscopic α -relaxation dynamics of polymers in supercooled states, we study the microscopic dynamics of a polybutadiene (PB) and silica nanoparticle mixture using QGS. The polymer dynamics can be studied in isolation because, at these timescales, the nanoparticles can be considered to be stable and only add a non-relaxing component to the intermediate scattering function. The experimental results show that the inter-chain α -relaxation time for the nanocomposite was slower than that for the pure PB in shallowly supercooled region.

2 Experiment

Two types of samples were used for the experiment: pure 1,4-*cis*trans PB and PB nanocomposite with silica nanoparticles. We prepared the PB (NF35R, Asahi Kasei) with a weight-average molecular weight (M_w) of 3.49×10^5 and a molecular weight distribution index (M_w/M_n) of 2.3. Here M_n is the number-average molecular weight of the rubber matrix. The percentages of *cis*, *trans* and *vinyl* in the PB were 35%, 52% and 13%, respectively. The PB nanocomposite was prepared with 20 volume% of silica nanoparticles with an average diameter of 100 nm (Seahoster, Nippon Shokubai) called PB-silica100. The PB and silica were mixed in an internal mixer until the temperature of the compound reached 423 K. After mixing, the nanocomposite sample was pressed into a sheet.

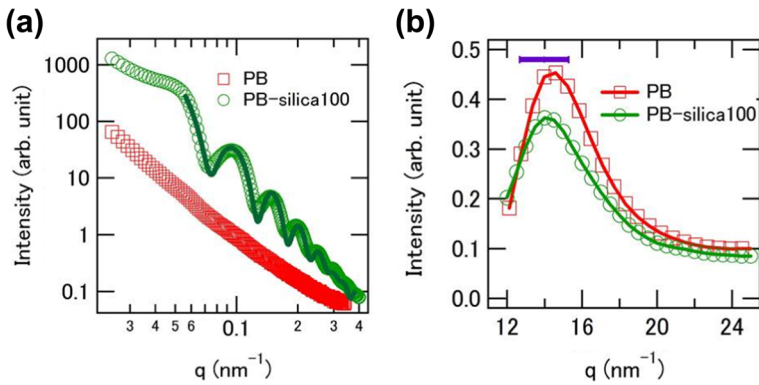


Fig. 1 SAXS and WAXS spectra. **a** SAXS spectra obtained for pure PB and PB-silica100 at room temperature with fitting curves. **b** WAXS spectra obtained for pure PB and PB-Si100 at room temperature. The bar represents the q region of the quasi-elastic scattering measurements; see the main text for further details

The glass transition temperature T_g of pure PB was determined to be ~ 180 K using differential scanning calorimetry (Q200, TA instruments) and no T_g difference could be detected among the two samples. In addition, to confirm the size of the nanoparticles, SAXS measurements were performed at the BL08B2 beamline at SPring-8 in Japan. QGS experiments were then performed using the nuclear resonant scattering beamline (BL09XU) at SPring-8. The energy width of the incident radiation was set to be ~ 3.5 meV at the excitation energy of the first nuclear excited state of ^{57}Fe using a high-resolution monochromator comprised of asymmetric Si (511) and Si (975) channel-cut crystals. The storage ring was operated in the several-bunch timing mode: 1/7-filling + several 5-bunch mode with bunch intervals of 684.3 ns. The emitters were ^{57}Fe -enriched ($> 96\%$) α -Fe foils. See Ref. 15 for the experimental details. Wide-angle X-ray scattering (WAXS) data were obtained between 12 and 25 nm^{-1} for pure PB and PB-silica100 at room temperature. The detector for the QGS measurements was placed in the inter-chain momentum transfer q region between 13 and 15 nm^{-1} , covering the first static structure factor peak located at ~ 14 nm^{-1} . For the pure PB and PB-silica100, QGS time spectra were measured at 220, 240 and 250 K. The sample temperature was controlled by a He-flow cryostat. Multi-element Si-avalanche photodiode detectors were used to detect the scattered gamma rays.

3 Results and discussion

Figure 1a and b show the obtained SAXS and WAXS data. First, we examined the SAXS data to determine the average silica nanoparticle diameter. We assumed that the q dependence of the scattering intensity $I(q)$ was $I(q) \propto \{3 [\sin(qR) - qR \cos(qR)] / (qR)^3\}^2$, where R is the silica nanoparticle radius [17]. The radius distribution was also taken into account. Because the silica nanoparticles were the main cause of the scattering observed in the SAXS data, we ignored the contribution of the polymer structure factor. The lines in Fig. 1a show the resulting fits. The average diameter of the silica nanoparticle obtained by fitting the SAXS data was 120 nm for PB-silica100. The result allowed us to determine the

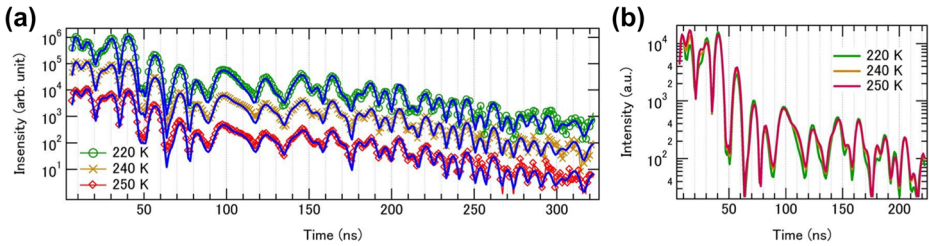


Fig. 2 Typical QGS time spectra and fitting curves. **a** Examples of time spectra obtained for PB-silica100 at 14 nm^{-1} at 220, 240 and 250 K. The error bars indicate the standard deviations and the lines show the fitting curves. **b** Comparison of the normalized fitting curves of the spectra obtained at each temperature suggesting the change of the spectrum shapes with increasing the temperature

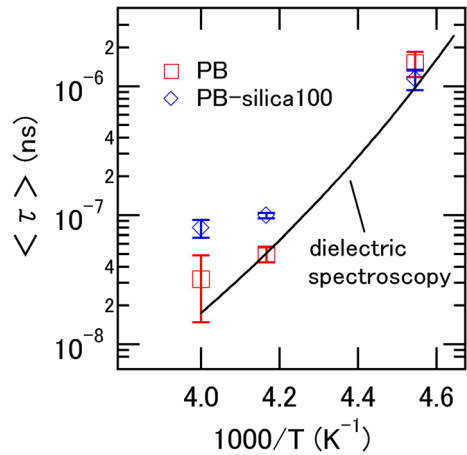
sizes of the nanoparticles mixed with the PB. From the WAXS results shown in Fig. 1b, we confirmed that the position of the main peak, which mainly reflects the inter-chain correlation of the PB, had changed very little and was covered by the q region in the quasi-elastic scattering measurements.

Examples of the time spectra obtained for PB-silica100 at 220, 240, and 250 K are shown in Fig. 2a. The shape of the spectrum is affected by the sample's normalised intermediate scattering function [15]. Least-squares fits were performed using the equations described in Ref. [15], and we assumed that the normalised intermediate scattering function was the Kohlrausch–Williams–Watts (KWW) function $F(q, t) = f(q) \exp\{-[t/\tau(q)]^{\beta_{\text{KWW}}(q)}\}$ for the pure PB case, where $f(q)$ is the relaxation amplitude, β_{KWW} is the stretching parameter, τ is the relaxation time, and t is the time. From the measurements on pure PB, the value of β_{KWW} was determined to be 0.48 ± 0.10 at $q \sim 14 \text{ nm}^{-1}$, which is consistent with the previously reported β_{KWW} value of 0.45 [18]. We obtained τ by setting β_{KWW} to be 0.45 for all the pure PB spectra and then calculated the mean relaxation time $\langle \tau \rangle$ from $\langle \tau \rangle = \tau \Gamma(1/\beta_{\text{KWW}}) / \beta_{\text{KWW}}$, where Γ is the gamma function [18].

Next, for the PB nanocomposites with silica nanoparticles, the polymer dynamics were studied by obtaining the relaxation time for the relaxing component in the normalised intermediate scattering function, accounting for the non-relaxing component originating from the stable nanoparticles. For nanocomposite systems, it is known that the polymer α -relaxation in the intermediate scattering function can be treated as a KWW function [3, 4]. We therefore used the function $F(q, t) = f(q) \exp\{-(t/\tau(q))^{\beta_{\text{KWW}}(q)}\} + c(q)$ to fit the normalised intermediate scattering function for the time spectra of PB-silica100, where $c(q)$ is the contribution of the non-relaxing component. By fitting the time spectra obtained for PB-silica100 at 250 K, we determined that the contribution of the non-relaxing component was $c = 0.22 \pm 0.07$ at the q value of the measurement assuming $\beta_{\text{KWW}} = 0.45$, which can be also confirmed by fitting. We used these values to analyse the time spectra obtained at other temperatures. In Fig. 2a, the obtained fitting curves are shown. In Fig. 2b, the normalized fitting curves of the spectra obtained at each temperature are shown. It can be visually confirmed that the spectrum shape changes with increasing the temperature.

The temperature dependence obtained for $\langle \tau \rangle$ is shown in Fig. 3. We found that, for pure PB, the temperature dependence showed a divergent behaviour (according to the Vogel–Fulcher–Tammann law) as previously observed for pure PB by QGS [16]. The previous study already revealed that, in the intra-molecular q region around 14 nm^{-1} , the relaxation is mainly caused by the diffusional inter-chain α -process [16]. We show the α -relaxation

Fig. 3 Temperature T dependence of relaxation time for pure PB and PB-silica100. Temperature dependence of the averaged relaxation times obtained for pure PB and PB-silica100 at $q \sim 14 \text{ nm}^{-1}$. The error bars indicate the standard deviations, and the line indicates the α -relaxation times obtained by dielectric spectroscopy [19]



time obtained by dielectric spectroscopy as a line in Fig. 3 demonstrating that our results are consistent with the results of dielectric spectroscopy [19].

The temperature dependence of $\langle \tau \rangle$ obtained for PB-silica100 also shows divergent behaviour although the parameters of the Vogel–Fulcher–Tammann law appear to be different from those for pure PB. This interesting difference in the temperature dependence will be investigated further in a future work, but we will discuss it qualitatively here. At 240 K, the α -relaxation time obtained at $q \sim 14 \text{ nm}^{-1}$ for PB-silica100 was longer than those for pure PB. This result is consistent with the conventional idea that the polymer α -relaxation time slows down due to interaction (chemical attachment and physical absorption) between the polymer and the silica nanoparticles [1, 2]. Furthermore, this difference is more evident in the higher temperature region comparing with that in 220 K suggesting that the presence of nanoparticles caused the polymer α -relaxation dynamics to clearly slow down in a shallowly supercooled state. Conversely, the presence of nanoparticles less causes a slowing down in a lower temperature region near T_g . This result is consistent with the fact that the presence of the silica nanoparticle doesn't largely change T_g as observed by the differential scanning calorimetry study. Further study on the nanocomposite system of PB and the silica nanoparticle such as the dependence of the polymer α -relaxation time on the size or concentration of the nanoparticle is required to elucidate the mechanism of the slowing down. The present result also shows that QGS can be used to reveal the polymer dynamics in nanocomposites and is appropriate for characterising their microscopic dynamics for the purpose of improving tyre performance.

4 Conclusions

In this paper, we have studied the effects of silica nanoparticles with diameter of 100 nm on the microscopic polymer dynamics using QGS. The results show that the presence of silica nanoparticles in the rubber caused the inter-chain α -relaxation dynamics of the polymer to slow down in a shallowly supercooled state. This suggests that the polymer α -relaxation dynamics were restricted by contact with the surfaces of the nanoparticles. Conversely, the presence of nanoparticles less causes a slowing down in a lower temperature region near T_g . Consequently, the presence of the silica nanoparticle doesn't largely change T_g of polymer as observed by the differential scanning calorimetry study.

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