X-ray Photon Correlation Spectroscopy of Silica Particles Grafted with Polymer Brush in Polystyrene Matrix

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Abstract. X-ray photon correlation spectroscopy system was setup at SPring-8, BL19LXU, and the partial coherence scattering data from the silica particles grafted with polymer brush in polystyrene matrix were measured. Firstly, the static speckle patterns were checked. Below the glass transition temperature of polystyrene (T_g), speckles were clearly observed, on the other hand, above T_g, the scattering patterns became smooth and speckles were hardly observed. These variances of the speckle patterns result from the particle motion. Secondly, from the time variance of the speckle data, time autocorrelation functions g²(q, t) are calculated. While the flat behaviour of g²(q, t) without relaxation were observed below T_g, the relaxation behavior with relaxation time ~10⁻⁰⁻¹⁰¹ were observed above T_g.

1. Introduction

Static and dynamic structures of nanoparticles in soft materials have received lots of interests from various view points. Studies using x-ray, small angle x-ray scattering for statics and x-ray photon correlation spectroscopy (XPCS) for dynamics [1,2,3,4], have been performed for investigating various interesting properties such as reinforcement of polymers or hyper diffusive motion near glass transition.

XPCS has been regarded as a powerful tool for revealing the dynamic structure of soft materials and the measurements are now routinely performed at ID1-10A of ESRF (France) and 8-ID of APS (U.S.A) using third-generation synchrotrons. But there is no dedicated beamline for XPCS in SPring-8, and very few papers [5] are found for performing XPCS. In this work, XPCS system was set up at SPring-8, BL19LXU (Hyogo, Japan), and the dynamic behavior of the polystyrene (PS)-grafted silica particles in PS matrix was investigated.

2. Experimental

The measurement was carried out at 27-m-long undulator beamline BL19LXU in SPring-8. Details of the beamline optics are presented elsewhere [6]. Figure 1 shows a schematic layout of the setup. The undulator source and the monochromator were tuned to an energy of 7.25 keV (λ = 1.71 Å) and higher harmonic x-rays were removed by the Pt-coated mirrors. The energy bandwidth of the Si(111)
monochromator leads to a longitudinal coherence length \( \xi_1 = \lambda^2 / \Delta \lambda \sim 1 \mu m \). The beam size of the light source was \( \sigma \sim 113 \times 14 (H \times V) \mu m^2 \), and the distance between the light source and the sample was \( R \sim 75 \text{ m} \). By calculating from the equation \( \xi_1 = \lambda R / (2 \pi \sigma) \), the transverse coherence length at the sample was to be obtained \( \xi_1 \sim 18 \times 146 (H \times V) \mu m^2 \). To ensure enough transverse coherence, we set a 20 \( \mu m \) diameter pinhole upstream 10 \( \text{m} \) of the sample. The parasitic scattering was cut by the 4-quadrant slits and the L-shaped slit, and the partially coherent x-ray was illuminated to the sample in vacuum. The typical flux at the sample was \( \sim 1 \times 10^{10} \text{ photons/sec} \). The scattered x-rays were detected \( \sim 3.5 \text{ m} \) downstream using a direct illuminated charge-coupled device (CCD) camera (PI-LCX 1300, Princeton Instruments) with 1340 \times 1300 pixels and a pixel size of 20 \( \mu m \). In this setting, a scattering vector of \( 2.4 \times 10^{-2} < q < 4 \times 10^{-1} \text{ nm}^{-1} \) was covered, where \( q = (4 \pi / \lambda) \sin \theta \) is the magnitude of the scattering vector, where \( \lambda \) and \( 2 \theta \) are the wavelength of X-rays and scattering angle, respectively. This \( q \)-range was small enough compared to the maximum of \( q \sim 1.6 \text{ nm}^{-1} \) estimated from the requirements for XPCS that \( \xi_1 \) should be smaller than the path difference. The time variance of the speckle data are measured in kinetics mode typically using 10 pixels wide window with \( \sim 130 \text{ frames per 300 and 1000 ms} \).

The sample preparation of PS-grafted silica particles in PS matrix will be briefly presented here [7]. The surface-initiator (2-bromo-2-methyl) propionyloxyhexyltriethoxysilane (BHE) was immobilized on silica nanoparticle (108 nm diameter; Nissan Chemicals) by solution method. Subsequently, polystyrene was grafted on silica nanoparticle using surface-initiated atom transfer radical polymerization with the ligand of \( N,N,N',N'',N''\)-pentamethyldiethylenetriamine in the solution of dimethylacetamide. The molecular weight of the grafted PS was \( M_n = 1.23 \times 10^5 \text{ g/mol} \), \( M_w/M_n=1.67 \), and the graft density was 0.95 chains/nm\(^2\). These particles were dispersed in polystyrene matrix

Figure 1. Schematic drawing of the experimental setup for XPCS at SPring-8, BL19LXU.

Figure 2. Scattering intensity profiles, obtained by slicing the 2-dimensional CCD images with total measurement time of \( \sim 2 \text{ minutes} \) at (a) 40 \( \text{C} \), (b)110 \( \text{C} \) and (c) 150 \( \text{C} \).
(\(M_w = 5.40 \times 10^4\), \(M_w/M_n=1.04\)). The content of the pure silica was 0.5 wt\%. The possibility of aggregation of nanoparticles was checked by small angle scattering down to \(q = 2.4 \times 10^{-2} \text{ nm}^{-1}\), near Guinier region, any aggregation features, such as intensity increasing at low-\(q\) region, are not observed.

3. Results and Discussion

Firstly the temperature dependence of speckle pattern is presented here. Figure 2 shows the scattering intensity profiles, obtained by slicing the 2-dimensional CCD images accumulated 120 times per exposure time 500 ms (total measurement time \(~2\) minutes) at 40 °C (a), 110 °C (b) and 150 °C (c). The profile at 40 °C (a) shows jaggy “speckle” pattern, which results from that the coherent scattered x-rays interfered at the detector. But the profiles at 110 °C (b) and 150 °C (c) are smooth and speckles are hard to be observed. These variances of the speckle patterns with increasing temperature result from the thermal motion of the silica particles as well as micro-Brownian motion of matrix PS. The silica particles in polystyrene were immobile below the glass transition temperature \((T_g)\) of polystyrene (~100 °C) and the speckles from the silica particles were clearly observed. But, above \(T_g\), the speckles moved because of the thermal motion of the silica particles, and the speckles were averaged during the measurement time.

The time-autocorrelation function \(g_2(q,t)\) for each pixels are calculated from the speckle data by
\[
g_2(q,t) = \frac{<I(q,t')I(q,t'+t)>}{<I(q,t')>^2},
\]
where \(I(q,t')\) is the scattered intensity at wave vector \(q\) and time \(t'\). The calculated \(g_2(q,t)\) are averaged over finite-sized regions in reciprocal space. The data at \(q=3.5 \times 10^{-2} \text{ nm}^{-1}\), at 40 °C (a), 110 °C (b) and 150 °C (c) are shown in Fig. 3 as representative data for the temperature dependence. At 40 °C, \(g_2(q,t)\) with sampling time of 300 ms and 1000 ms are flat around the value of unity. Same behavior is also shown at every \(q\) at 40 °C. These results indicate that the sample is in static state at 40 °C (<\(T_g\)) and the period over which the synchrotron and our setup are sufficiently stable. On the other hand, at 110 and 150 °C, \(g_2(q,t)\) shows non-flat behavior. Since these temperatures are higher than \(T_g\), these behavior are considered to reflect the motion of the silica particles. Autocorrelation functions for soft glassy material are often by the stretched exponential expression,
\[
g_2(q,t) = A\exp[-2(t/\tau)\beta]+1,
\]
Figure 3. Autocorrelation functions \(g_2(q,t)\) at \(q=3.5 \times 10^{-2} \text{ nm}^{-1}\). The measured temperatures are (a) 40 °C, (b) 110 °C and (c)150 °C. Open circles and solid circles are corresponding to the sampling time of 300 and 1000 ms respectively. Solid lines in (b) and (c) are fitting curves by Eq. (2).

Figure 4. Relaxation time \(\tau\) plotted against \(q\) for 110 °C (open circles) and 150 °C (solid circles). The solid curves are fitting curves by \(\tau = A/q \beta\). The dashed line calculated from simple Brownian behaviour model.
where $\beta$ quantifies the deviation from exponential relaxation, $\beta = 1$ corresponding to the behavior of particles like noninteracting Brownian motion in a Newtonian liquid, and $\tau$ the relaxation time. The prefactor $A$, speckle contrast, is small compared with the ideal value of 2. This speckle contrast depends on the values of the beam’s coherence, the scattering vector and so forth. Calculated from the static speckle patterns, the speckle contrast at $q = 3.5 \times 10^{-2} \text{nm}^{-1}$ is $\sim 1.03$. This is fairly consistent with the value of $A$. But the small value compared with 1.03 may indicate the existence of faster mode. By fitting measured $g_2(q,t)$ at $3.5 \times 10^{-2} \text{nm}^{-1}$ by Eq. (2), $\beta = 2.44$, $\tau = 37.5 \text{s}$ at 110 °C and $\beta = 2.26$, $\tau = 1.47 \text{s}$ at 150 °C are obtained. At other $q (2.6 \times 10^{-2} < q < 6.5 \times 10^{-2} \text{nm}^{-1})$, $\beta > 1$ are also obtained. The relationship $\beta > 1$ in equilibrium system in “soft solids” has been indicated by many experiments [1,2,3,4], and such behavior is considered to be resulted from hyperdiffusion or ballistic motion. In the literatures, the relationship $\beta < 2$ is common feature. Compared with the values in the literatures, the present values are a little larger. The present observation may indicate the effect of faster modes or another kind of motions, now the possibilities of the sedimentation or the flowing phenomena of the particles are not ruled out. In Fig. 4, $\tau$ against $q$ at 110 and 150 °C are plotted. There is a slight decrease with increasing $q$ both at 110 and 150 °C. The fitting procedure by $\tau = C / q$, which is sometimes performed for the data with $\beta > 1$, is done as shown in Fig.4. The fitting results look sufficient, but the validity of the fitting is not argued here because the present data may not include enough number of plots.

4. Conclusion

XPCS system was set up at SPring-8, BL19LXU, and the dynamics of the polystyrene grafted silica particles in polystyrene matrix was measured. Firstly, the static speckle patterns were checked with total measurement time of ~2 minutes. At 40 °C (<$T_g$), speckles were clearly observed, but, at 110 and 150 °C (> $T_g$), the speckles were disappeared and the smooth intensity patterns were observed. These variations of the speckle patterns result from the particle motion. Secondly, from the time dependence of the speckle data, time autocorrelation functions $g_2(q,t)$ are calculated. In $g_2(q,t)$, while flat behavior without relaxation were observed below $T_g$, the relaxation behavior with $\tau \sim 10^2 - 10^3$ were observed above $T_g$. In the present work, we successfully observed the dynamics of the silica particles in PS matrix by XPCS, but the more measurement data are necessary for the detailed discussions.

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