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Letter

# Nanoscale Particle Motion Reveals Polymer Mobility Gradient in **Nanocomposites**

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S Supporting Information

ABSTRACT: Polymer mobility near nanoparticle surfaces has been extensively discussed; however, direct experimental observation in the nanocomposite melts has been a difficult task. Here, by taking advantage of large dynamical asymmetry between the miscible matrix and surfacebound polymers, we highlighted their interphases and studied the resulting effect on the nanoparticle relaxation using X-ray photon correlation spectroscopy. The local mobility gradient is signified by an unprecedented increase in the relaxation time at length scales on the order of polymer radius of gyration. The effect is accompanied by a transition from simple diffusive to subdiffusive behavior in accord with viscous and



entangled dynamics of polymers in the matrix and in the interphase, respectively. Our results demonstrate that the nanoparticleinduced polymer mobility changes in the interphases of nanocomposite melts can be extracted from the length-scale-dependent slow particle motion.

ynamics at nanoparticle (NP)-polymer interfaces is linked to the unusual rheological properties of polymer nanocomposites (PNCs);<sup>1-3</sup> the details of such a correlation are not well-understood. Polymers confined in thin film geometries display a structure and dynamics that can be very different from the bulk.<sup>4-6</sup> Similarly, a favorable polymernanoparticle interaction immobilizes the chains on the NP surfaces' and forms a confined interfacial layer accompanied by a transition phase (i.e., interphase) with a mobility gradient toward the bulk. Despite being of utmost importance for both fundamental physics and engineering the transport properties of advanced nanocomposite materials, the spatial extent and the complex dynamics of the interphases is not well known.

Various techniques have, therefore, been employed. For example, Cheng et al.8 used atomic force microscopy to visualize the interfacial layer in glassy PNCs (in which the NPs are immobilized) and Brillion light scattering revealed the elastic modulus of a polymer twice larger at the  $\sim 2-3$  nm thick interface compared to the bulk. In the melt state, however, direct observation of the changes in the polymer dynamics in the vicinity of mobile NPs is an extremely difficult task. Conventional techniques, such as dielectric and mechanical spectroscopy,<sup>9-11</sup> lack appropriate spatial resolution, thus, providing polymer behavior averaged from the bulk and the interphase, which requires detailed modeling and assumptions. On the other hand, high resolution neutron spectroscopy (specifically quasielastic backscattering) allows direct observation of the segmental dynamics in nanocomposite melts. It was shown that the attractive interaction between a polymer and NPs slows down the overall segmental dynamics in nanocomposite melts.<sup>12</sup> The length-scale of quasielastic neutron spectroscopy is yet restricted to very short distances (typically below several nm's) and the time scale is rather fast (typically faster than ns)<sup>13</sup> compared to the longest relaxation time of the polymers, which essentially controls the viscosity. Therefore, a direct link between the modified segmental dynamics and the spatial variation of the polymer mobility within the interphases has not been possible.

Here, we used X-ray photon correlation spectroscopy (XPCS) and investigated the slow NP relaxation, instead of that of the polymer, at time scales from a few hundred milliseconds to tens of seconds. Since the NP motion is essentially directed by the local polymer viscosity, we hypothesize that the polymer mobility gradient (if there is any) around the NPs can be decoded from the NP dynamics itself.

We considered two nanocomposite systems: (i)  $SiO_2$  NPs dispersed in a low- $T_g$  poly(ethylene oxide) (PEO,  $T_{g,PEO} \approx 210$ K), representing a model attractive PNC system, (ii) SiO<sub>2</sub> NPs coated with a high- $T_g$  poly(methyl methacrylate) (PMMA,  $T_{g,PMMA} \approx 400 \text{ K}$ ) and dispersed in the low- $T_g$  PEO matrix. In the latter, PEO and PMMA form a neutral interface since the Flory-Huggins parameter is negligibly small.<sup>14</sup> The large  $T_{\sigma}$ difference between them enhances the viscosity contrast between the interface and matrix and allowed us to identify,

Received: March 9, 2019 Accepted: April 29, 2019 Published: May 1, 2019

for the first time, the mobility gradient around NPs from the length-scale-dependent NPs relaxation.

The hydrogenated PEO (*h*-PEO,  $M_w = 35 \text{ kg/mol}, M_w/M_p =$ 1.08) and the deuterated PEO (d-PEO,  $M_w$ = 35 kg/mol,  $M_w$ /  $M_{\rm p}$ = 1.09) were purchased from Polymer Source Inc. *h*-PMMA  $(M_{\rm w} = 98.5 \text{ kg/mol}, M_{\rm w}/M_{\rm n} = 1.08)$  was purchased from Sigma-Aldrich. Both polymers are well-above the entanglement molar masses (2 kg/mol for PEO and 18 kg/mol for PMMA<sup>15</sup>). The polymers were dried further under vacuum at 363 K for 12 h prior to use. The colloidal silica NPs ( $\approx 25$ nm in radius with a size polydispersity  $\approx 0.3$ ) in methyl ethyl ketone were supplied by Nissan Chemicals America and used as received. The PNCs were prepared according to the protocol described elsewhere.<sup>16</sup> The PNCs with PMMAcoated NPs were prepared using a protocol similar to bare NP PNC preparation. The final NP concentration was determined from thermogravimetric analysis to be 4% and 5% (by volume), corresponding to face-to-face interparticle distances (IDs) of 67 and 75 nm for the bare NPs and the PMMAcoated NPs, respectively. Note that the radius of gyration,  $R_{g}$ , of 35 kg/mol PEO melt is  $\approx 6.8$  nm,<sup>15</sup> 10× smaller than the IDs.

In both PNC samples, the presence of a bound polymer layer (BL), either PEO or PMMA, provides steric protection against NP aggregation. The SAXS data in Figure 1A shows no



**Figure 1.** (A) SAXS profiles (shifted vertically for clarity) from the PNCs at different temperatures. The lines are for PNCs with bare NPs and the dashed lines are for PNCs with PMMA-coated NPs. The inset shows the deviations of the profiles obtained by dividing the SAXS intensities of the coated particles by the bare NPs,  $I^{\rm N}(Q)$ . (B) Temperature-dependent Kratky plots from the SANS profiles of the PMMA-coated NPs in the PEO matrix that is contrast matched to the NPs. The arrows in SAXS and SANS indicate the location of the bound layer correlations.

low-Q upturn in the intensity, confirming aggregate-free dispersion of both bare NPs (shown as lines) and PMMAcoated NPs (shown as dashed lines) in PEO matrices. There is a clear difference between the profiles at intermediate and low-Q, which we display in the inset by dividing the intensity from the coated NPs by the intensity of the bare NPs,  $I^N(Q)$ . The peak at  $Q \approx 0.01$  Å<sup>-1</sup> corresponds to a length-scale  $\approx 60$  nm, close to NP diameter, and can be due to the PMMA BL, which has a different electron density than the matrix PEO. Notice also that the location of the peak is essentially temperatureindependent; however, the deviations of the profiles from the bare NPs and PMMA-coated NPs at low Q become smaller at elevated temperatures. This suggests an enhanced intermixing of PEO and PMMA at elevated temperatures, which reduces the X-ray contrast between the BL and the matrix.

The BL correlation peaks are more apparent in small-angle neutron scattering (SANS),<sup>17</sup> which we performed on the

NG30B beamline at National Institute of Standards and Technology Center for Neutron Research (NIST-NCNR). We minimized the particle contribution to scattering intensity in the intermediate and high-Q by using a mixture of d-PEO and *h*-PEO (d/h: 52/48 ratio) matrix that matches with the scattering length density of SiO<sub>2</sub> nanoparticles; the *h*-PMMA BL is therefore highlighted. The details of the SANS experiments and analysis are given in the Supporting Information. Figure 1B shows the Kratky plot  $(IQ^2 \text{ vs } Q)$  for the h-PMMA-coated NPs in the contrast matched matrix. At high Q, the intensity is due to the PEO chains, which shows the usual Debye plateau. At intermediate and low-Q, the contribution from the *h*-PMMA interfacial layer results in a correlation peak at  $Q \approx 0.01$  Å<sup>-1</sup>, similar to the SAXS result. Its intensity appears to significantly decrease with temperature, and, at T = 423 K, results in a profile that is similar to the bare NP composites where the BL is less visible (see the profiles for the neat and the PMMA-coated NPs in Supporting Information). This suggests a decrease of scattering contrast within the interphases due to enhanced mixing of h-PMMA with d/h PEO chains with temperature, as SAXS data also suggested and in parallel with the thermal-stiffening nature of these nanocomposites.<sup>16,18</sup>

We then looked at the slow NP motion, which is directed by the local viscosity of the medium. We performed XPCS experiments on beamline 8-ID-I at the Advanced Photon Source at Argonne National Laboratory. The normalized intensity-intensity autocorrelation function,  $g_2$  (Q,t), was obtained over the wave vector range 0.003 Å<sup>-1</sup> < Q < 0.02 Å<sup>-1</sup>, corresponding to the length-scale  $\approx 20-200$  nm. The correlation function is related to the intermediate scattering function (ISF),  $f(Q_t)$ , as  $g_2(Q_t) \sim 1 + A \cdot [f(Q_t)]^2$ , with A and *t* being the Siegert factor of the instrument and the delay time, respectively. The correlation functions at all length-scales for bare NPs and PMMA-coated NPs in PEO at 393 K are shown in Supporting Information. The  $g_2$ s for the bare NPs are nearly exponential, and the relaxation time monotonically decreases with increasing Q, as expected. In contrast, the behavior of the PMMA-coated NPs is nonmonotonic: at low-Q it behaves similar to bare NPs, and at higher Q, the relaxation becomes remarkably stretched with the time scale shifted to longer values.

To gain further insight, the ISF was best fit to the stretched/ compressed exponential functions,  $f(Q_t) = \exp[-(t/\tau)^{\beta}]$ , with relaxation time,  $\tau$ , and the stretching/compressing exponent,  $\beta$ . Figure 2 shows the bare NPs exhibit a diffusive motion with  $\tau$  $\propto Q^{-2}$  scaling with  $\beta$  above and close to unity and move faster at higher temperatures. Diffusive motion for bare NPs is expected. In a previous work, Guo et al.<sup>19</sup> showed that the tracer NPs in unentangling polystyrene melt exhibit simple diffusion at  $T > 1.2T_{e}$ , whereas hyperdiffusive motion was observed at lower T, close to the  $T_g$  of the matrix. Since the longest relaxation time of PEO at the experimental temperatures  $(T > 1.7T_g, PEO)$  falls well below the shortest XPCS time  $(t_{XPCS} > 10 \text{ ms} > t_d)$  where  $t_d$  is the terminal relaxation time<sup>16</sup>), the entanglements of PEO are relaxed and the particle motion is directed by the bulk viscous motion of the matrix;therefore, NPs exhibit simple diffusion.

The nonmonotonic relaxation of PMMA-coated NPs in the same PEO matrix is apparent in the Q dependence of  $\tau$  and  $\beta$ . At large distances (low Q), the scaling  $\tau \propto Q^{-2}$  and  $\beta \approx 1$  suggests that these NPs also exhibit simple diffusion in the PEO matrix, similar to the bare NPs. The diffusive motion



**Figure 2.** Relaxation times  $(\tau)$  and stretching exponents  $(\beta)$  for bare NPs (shown by open symbols) and PMMA-coated NPs (shown by filled symbols) at different temperatures. The line shows the scaling of the relaxation time with the wave-vector for a simple diffusive motion (i.e.,  $\tau \propto Q^{-2}$ ). Similar results are obtained for the average relaxation time  $\langle \tau \rangle = (\tau/\beta)\Gamma(1/\beta)$ , with  $\Gamma$  being the gamma function, as shown in the SI.

holds up to  $Q \approx 0.007$  Å<sup>-1</sup> (corresponding length-scales around 90 nm), above which  $\tau$  monotonically increases with Q. As the length-scale probed gets shorter, the NPs feel the effect of the less-mobile interfacial PMMA layer. This is clearly different from the behavior of bare NPs; the observed stiffening at the nanoscale is due to the mobility gradient induced by the bound PMMA layer. To our best knowledge, such an unusual NP relaxation has not been observed before. The increase in  $\tau$  with *Q* is accompanied by the decrease of  $\beta$ . The stretched exponential relaxation,  $\beta < 1$ , at high-Q is a signature of a subdiffusive NP motion, which is dictated by the entanglements in polymeric liquids, as previously shown by Guo et al.<sup>20</sup> and Poling-Skutvit et al.<sup>21</sup> As mentioned earlier, the entanglements are relaxed (in the time-scale of XPCS) for the PEO matrix, however, the entanglement relaxation time for PMMA is extremely long (hundreds of seconds) around its  $T_{o}$ ; therefore, the NP motion gets increasingly subdiffusive as shorter length-scales are probed.

The temperature-dependent SAXS and SANS profiles suggested an enhanced intermixing of the PEO matrix with interfacial PMMA at elevated temperatures. The transition between the matrix-dominated and the interphase-controlled regions gets broader with less strong upturn of  $\tau$  at 433 K (above  $T_{g,PMMA}$ ). Note, however, that the stretching exponent for PMMA-coated NPs is not significantly affected by temperature; the NP motion is still governed by the entangled dynamics within interphases at high Q and at all T investigated.

The length-scale-dependent NP mobility can be more quantitatively evaluated from the mean-square displacements (MSD). As the XPCS signal is collective in nature, the probed dynamics is related to the relative motion of the NPs with respect to each other; however, at Q values above the first structure factor peak, that is, for length scales smaller than the interparticle distance, the dynamics probed is mostly the single particle one. Therefore, the ISF can be related to a relative effective, Q- and t-dependent,  $MSD_{eff}$  by  $f(Q, t) = \exp\left(-\frac{\langle [r(Q,t)]^2 \rangle_{eff}}{6}Q^2\right)$  within the Gaussian approximation.<sup>21</sup> Figure 3 compares  $\langle [r(Q,t)]^2 \rangle_{eff}$  for the bare and the PMMA-coated NPs in PEO at 363 K. The scaling



**Figure 3.** Relative effective mean square displacements,  $\langle [r(Q,t)]^2 \rangle_{\text{eff}}$  as a function of time for (A) the bare NPs and (B) for the PMMA-coated NPs at different Q values at 363 K.

 $\langle [r(Q,t)]^2 \rangle_{\text{eff}}$ :  $t^{1.0}$  is a signature of diffusive behavior and holds for the bare NPs for all Q, whereas it applies for the PMMA-coated NPs only at low-Q. When increasing Q for the PMMA-coated NP, MSD transitions from  $\approx t^{1.0}$  toward  $\approx t^{0.5}$  scaling; characteristic of subdiffusive motion becomes more apparent at longer times.

At the low-Q regime of Figure 2, the calculated viscosity values from the XPCS relaxation time and using the Stokes– Einstein relation,  $\eta_{\rm XPCS} = k_{\rm B}T/[6\pi D_{\rm eff}(Q \rightarrow 0)R_{\rm NP}]$ , with an effective diffusion coefficient defined as  $D_{\rm eff}(Q) = 1/[\tau(Q)/Q^2]$ , are close to the bulk viscosity of PEO<sup>22</sup> for the bare NPs. The temperature dependence of the local viscosity is also well-described by Vogel–Fulcher–Tamman (VFT) equation,  $\eta(T) = \eta_{\rm o} \exp[B/(T - T_{\infty})]$  with known B = 1090 and  $T_{\rm o} = 155$  K for bulk PEO<sup>22,23</sup> (shown in Figure 4A). The attractive bare



**Figure 4.** (A) Temperature dependence of the matrix viscosity experienced by the NPs at low-*Q*. The open and filled symbols are for the bare NPs and the PMMA-coated NPs, respectively. The line is the VFT prediction for the neat PEO. The inset images illustrate the motion of NPs with and without PMMA layer. (B) The effective diffusion coefficient for the bare NPs and the PMMA-coated NPs as a function of the length-scale probed relative to the NP size.

NPs, therefore, do not affect the properties of the matrix polymer away from the interface. Starr et al.<sup>24</sup> reached a similar conclusion from their theoretical study on strongly attractive polymer nanocomposites, which indicated that the BL "cloaks" nanoparticles; hence, the dynamics of the matrix remains unaffected. This is in contrast to PMMA-coated NPs at low Q, where the calculated local viscosities are  $\approx 2 \times$  lower than the bulk viscosity of PEO (Figure 4A). We attribute this to negligible enthalpic interaction between the PMMA layer and PEO matrix; the PMMA-coated NPs essentially create neutral interfaces for the PEO matrix, which is akin to free surfaces. In their XPCS work, Koga et al.<sup>6</sup> showed the free surface of thin films to be less entangled than the bulk chains. Similar to this argument, the PEO can be disentangled in the presence of well-dispersed neutral/repulsive interfaces, which in this case resulted in a 2-fold decrease in the viscosity experienced by the PMMA-coated NPs. This is in line with the disentanglement of PEO matrix chains in the presence of the PMMA interfacial layer observed in neutron spin-echo in a previous work.<sup>16</sup>

In the high-Q regime, where the interphase effects dominate, the estimation of viscosity from subdiffusive motion is not readily possible. Instead, we compared the Q-dependence of the effective diffusion coefficient. Figure 4B shows  $D_{\rm eff}$  as a function of the probed length scale,  $\delta = 2\pi/Q$  relative to the particle size  $(D_p)$ , representing the distance from the NP surface. The mobility gradient around the PMMA-coated NPs is clear. At short distances, $D_{eff}$ s are lower by nearly an order of magnitude and tend to converge as high- $T_{\rm g}$  PMMA interface layer is approached. The measurement temperature has pronounced effect on the plateau region and the transition from interphase to the bulk gets broader with temperature. At 363 K, the transition occurs over a length-scale  $\approx$ 20 nm, a distance  $\approx 2 \times$  larger than  $R_g$  of PMMA, whereas at 433 K, the transition is broader,  $\approx$ 40 nm, corresponding to a distance that is  $\approx 4 \times$  larger than  $R_{g,PMMA}$ . Previous studies on the nanoparticle dynamics and chain diffusion also inferred that the effect of attractive interfaces can propagate to distances as large as 8  $R_{\rm g}$  of the bulk chains.<sup>25–27</sup> In contrast to the PMMAcoated NPs, the mobility gradient for the bare NPs in the neat PEO matrix is not appreciable well above the  $T_{\sigma}$  of the PEO.

The results clearly showed that functionalization of the NP surfaces with a high- $T_{\sigma}$  polymer that is miscible with the low- $T_{g}$  matrix enhanced the viscosity contrast between the interfacial and the bulk chains and allowed access to the mobility gradients. It is noteworthy here that we considered particle sizes larger than the chain size (and entanglement mesh size;  $R \approx 25$  nm  $\gg R_g \approx 7$  nm); therefore, the recent discussions on the NP size effect<sup>28–30</sup> are not relevant in this work, and the observed dynamical changes are due to interfaces only. We believe, however, that using smaller NPs would allow accessing mobility gradients even closer to NPs surfaces, provided that the size effects are carefully taken into account. Furthermore, our matrix polymer was well above the  $T_{\rm g}$  in the liquid state, with no entanglement effects. This study can be extended to higher  $T_g$  polymer matrices so that the interface effects on the dynamic heterogeneities associated with the glass transition can also be extracted from hyperdiffusive relaxation of NPs.<sup>19,31</sup> Also, as the interphase is strongly dependent on the polymer conformation on NPs, we conjecture that the effect of polymer grafting on the degree of interfacial entanglements and the mobility gradients within the graft layer<sup>32</sup> can also reflect on the slow NP dynamics. In all cases, though, individual dispersion of NPs in polymers,

either in melt state or solution, is essential to eliminate any contribution from particle caging or morphological effects.<sup>33,34</sup> The dispersion stability of our samples is shown in the SI.

In conclusion, we investigated the slow motion of welldispersed nanoparticles in polymer melts using XPCS. The mobility gradient around NPs is reflected as an entanglementcontrolled subdiffusive motion with a characteristic relaxation time increasing with decreasing probed-length scales. The small-angle scattering and the temperature-dependent NP dynamics demonstrated that the long-debated questions on the dynamics and the spatial extent of the interphases in polymer nanocomposite melts can be well-studied from the lengthscale-dependent NP motion. We conjecture that our results will stimulate new theoretical and experimental studies concerning the polymer dynamics near nanoparticle surfaces that is linked to the macroscopic rheological properties of advanced nanocomposites.

## ASSOCIATED CONTENT

## **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacro-lett.9b00176.

SANS intensity profiles and representative correlation plots (PDF)

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#### **Author Contributions**

The manuscript was written through contributions of all authors.

# Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work utilized facilities supported in part by the National Science Foundation under Grant No. DMR-1508249 and used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. The identification of any commercial product or trade name does not imply endorsement or recommendation by the National Institute of Standards and Technology. Throughout the paper, error bars represent one standard deviation.

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