# Structure and Entanglement Factors on Dynamics of Polymer-Grafted Nanoparticles

Siqi Liu[†], Erkan Senses[†], Yang Jiao[†], Suresh Narayanan[§], and Pinar Akcora[†,*]

[†]Department of Chemical Engineering and Materials Science
Stevens Institute of Technology, Hoboken, NJ 07030, United States

[§]Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, United States

## ABSTRACT

Nanoparticles functionalized with long polymer chains at low graft density are interesting systems to study structure-dynamic relationships in polymer nanocomposites since they are shown to aggregate into strings in both solution and melts, and also into spheres and branched aggregates in the presence of free polymer chains. This work investigates structure and entanglement effects in composites of polystyrene grafted iron oxide nanoparticles by measuring particle relaxations using X-ray photon correlation spectroscopy. Particles within highly ordered strings and aggregated systems experience a dynamically heterogeneous environment displaying hyper-diffusive relaxation commonly observed in jammed soft glassy systems. Furthermore, particle dynamics is diffusive for branched aggregated structures which could be caused by less penetration of long matrix chains into brushes. These results suggest that particle motion is dictated by the strong interactions of chains grafted at low density with the host matrix polymer.

Rheological properties of polymer nanocomposites provide valuable information on the role of interactions between functionalized nanoparticles and polymer media. As new functionalized nanoparticles are being developed, such as polymer-grafted nanoparticles, there is still little known about how transport properties of any solute can be controlled with the inner structure and dynamics of bulk composites. Dynamics of nanoparticles is commonly used to resolve fundamental problems such as measuring the viscous properties of thin films, dynamics of free surfaces and confined interfaces from the diffusion of particles[1-7] or to explore the heterogeneous mechanical environments[8,9]. Since elastic properties are dependent on both the aggregation state of particles and the interactions between grafted and free matrix chains, particle relaxations can provide physical insight into the role of interfaces on mechanical properties. In composites with similar dispersion states, which were studied in transmission electron microscopy and small-angle X-ray scattering experiments, entropic interactions of grafted chains with different lengths of matrix chains were shown to be different[10]. Subsequently, these interactions were modified by applying oscillatory shear flows[11]. In this study, we report the particle dynamics of structurally and rheologically well-studied polystyrene (PS)-grafted iron oxide nanoparticles in PS matrices. We reported in our previous works that nanoparticles with long graft chains form strings both in solution and in their chemically identical matrix homopolymer[12]. Particles with shorter grafts, however, form branched aggregates, spheres and well-dispersed particles[12] as graft density is varied from 0.017 to 0.12 chains/nm$^2$. X-ray photon correlation spectroscopic (XPCS) experiments on these structured nanocomposites showed that string forming particles followed heterogeneous dynamics, and short brush sample with less entropic interactions with long matrix chains, behaved diffusive. Herein, these XPCS results are discussed in conjunction with their previously reported rheological and structural results[10-12].

There is significant interest in exploring dynamics of interfaces and thin films by probing motions of a marker in XPCS technique[1]. Gold nanoparticles have been used to probe the entanglement dynamics of polymer chains[1,3]. A $\tau \propto q^{-1}$ relationship in entangled polystyrene thin films was attributed to elastic networks provided by viscoelastic effects of entangled polymer melt[3]. The sub-diffusive behavior of the gold particles was explained in terms of the ratio of entanglement mesh and particle size[8]. It was suggested that particles in the entanglement mesh feel the fluctuations of chains, thus move in a sub-diffusive manner[8]. Hyper-diffusive dynamics can be originated from strain motion caused by local heterogeneous stress relaxations[2,13] and is widely observed in soft glassy materials. In a polymer-grafted nanoparticle system, it was proposed that hyper-diffusive dynamics arises from nonequilibrium states[14]. It was suggested that thermal fluctuations in a nonequilibrium state produce a strain field that would yield hyper-diffusion of suspended polymer-grafted particles that is akin to gels[13,15]. Dynamics of star polymers has been investigated as well to reveal the effect of the number of arms on relaxations[16,17]. It was reported that at low number of arms, two step relaxations appear due to higher attractive interactions between particle cores[18].

In this work, we present particle dynamics in composites with known structures and rheology to reveal the role of soft particle-matrix interactions by probing particle relaxations. We prepared composites from particles of the same grafting density in different molecular weights and showed that matrix chains did not govern the aggregation of particles[12]. We applied oscillatory shear on these samples to observe whether entanglements between brush and matrix chains result in some constraints to disentanglement and create a network of entangled chains. The nonlinear rheology experiments showed that grafted chains of the same length soften in short matrix chains and stiffen in long matrix chains in large amplitude oscillatory shear[11]. These unusual results indicate that the mechanical response of composites prepared with functionalized particles changes with the evolution of entanglements between grafts and matrix. It is important to note that synthesis of functionalized particles and their structural characterization and rheological properties were described in prior works[10,11,12]. In this paper, we underline the importance of entanglement between matrix and low-graft density chains on relaxations of nanoparticles.

**Table 1**: Sample specifications and XPCS experiment temperatures

| **Sample name** | **Graft Mw [kg/mol]** ($M_w/M_n$) | **Matrix Mw [kg/mol]** ($M_w/M_n$) | **Graft density [chains/nm$^2$]** | **Particle core loading [wt%] (Volume fraction of grafted nanoparticles [vol%])** | **Structure** | **XPCS temperature [°C]** |
|---|---|---|---|---|---|---|
| A | 43 (1.05) | 124 (1.28) | 0.017 ± 0.004 | 5 (2) | branched | 183.2 |
| B | 43 (1.05) | 43 (1.05) | 0.017 ± 0.004 | 5 (2) | branched | 152.4 |
| C | 119 (1.07) | 40.5 (1.11) | 0.016 ± 0.004 | 5 (3.5) | strings | 150.0 |
| D | 119 (1.07) | 100.5 (1.09) | 0.016 ± 0.004 | 5 (3.5) | strings | 175.8 |
| E | 100 (1.07) | 130 (1.08) | 0.074 ± 0.02 | 15 (34.3) | dispersed | 185.0 |
| F | 45 (1.11) | 130 (1.08) | 0.12 ± 0.04 | 15 (26.0) | dispersed | 185.0 |
| G | 45 (1.11) | 130 (1.08) | 0.057 ± 0.002 | 15 (14.2) | spheres | 185.0 |

The protocol for preparation of polymer grafting onto iron oxide nanoparticles is published in our previous works[11,12]. Polystyrene of 124 kg/mol and 43 kg/mol molecular weights were grafted on 8-nm nanoparticles (in diameter) to achieve different grafting densities as listed in Table 1. The grafted particles were then mixed with the host 43 kg/mol or 124 kg/mol polystyrene matrices, sonicated for 20 s, cast in Teflon cups and dried in air to prepare films. Films were then annealed at 150$^o$C under vacuum for 2 days. Composites were molded into 1-

mm diameter holes on aluminum sample holders under compression and annealed at 180$^{o}$C for XPCS measurements.

XPCS measurements were performed at the 8-ID-I beamline of the Advanced Photon Source at Argonne National Laboratory. Sample areas of 20 μm x 20 μm were illuminated by coherent X-rays with photon energy of 11 keV. The normalized intensity-intensity autocorrelation function was obtained over the wave vector range 0.027 nm$^{-1}$< q < 0.3 nm$^{-1}$ at 18 discrete q. Samples were held at the desired temperature for 20 min to attain thermal equilibrium. Data was collected at five different locations for each sample to ensure uniformity and stability of the particle dispersion, both in structure and dynamics. The measured intensity autocorrelation function, $g_2 = 1 + Af^2(q,t)$ which is related to the dynamic scattering function, $f(q,t) = \exp[-(t/\tau)^{\beta}]$, were fit to a stretched exponential model. We compare the relaxation times ($\tau$) and stretching exponent ($\beta$) in discussing the relaxations of our samples. Characteristic diffusive dynamics is presented with $\tau \sim q^{-2}$ relationship, and hyper-diffusive relaxation time scales inversely with wave vector $q$ as $\tau \sim q^{-\alpha}$, where 1<α<2.

We first discuss the XPCS results of the samples circled in Figure S1. These two samples are selected as they present similar particle structures (branched aggregates) in different matrix molecular weights but particle dynamics changes from diffusive to hyper-diffusive. Because relaxations of 43 and 124 kg/mol matrix chains are different, we performed the XPCS measurements at different temperatures (Table 1) to match the viscosity of matrix chains. We used the William-Landel-Ferry (WLF) equation to choose XPCS measurement temperatures: $log(\frac{\eta_{o,T}}{\eta_{o,T_{ref}}}) = \frac{-C_1(T - T_{ref})}{C_2 + (T - T_{ref})}$. $C_1$ and $C_2$ are constants determined from the rheological shift factors for a time-temperature-superposition of the rheological data at 170$^{o}$C. The corresponding viscosity at 170$^{o}$C for 130 kg/mol PS was found to be $\eta_{o,\mathrm{ref}}$ = 24,000 Pa-s with $C_1$ = 5.98 and $C_2$ = 124. Figure S2 shows that viscosity of different matrix molecular weights (43, 100, 124 and 130 kg/mol PS matrix chains) was matched at 5430 Pa-s by adjusting temperature for each sample to diminish temperature dependent relaxation of composites. Note that our XPCS experiment temperatures are well above the $1.2T_g$ of PS. We were careful in this, because in a recent work, PS-grafted nanoparticles was measured in XPCS around $T_g$ of PS, in which hyperdiffusivity of particles has been attributed to dynamic heterogeneities associated with the glass transition[19].

Figure 1 shows that PS (43 kg/mol)-grafted nanoparticles follow diffusive dynamics in 124 kg/mol PS matrix (Sample A) with $\tau \sim q^{-2}$ dependence with $\beta$ reaching to 1. In the case of 43 kg/mol PS matrix (Sample B), particles follow hyper-diffusive dynamics with $\beta$ values between $1< \beta < 1.5$. We deformed Sample A in oscillatory shear mode at 100% strain and 1 rad/s at 150$^{o}$C in an ARES G2 rheometer as prescribed in Reference[11]; and found by XPCS that dynamics becomes hyper-diffusive and $\beta$ switches to 1.5. Since we showed that aggregated particle structures do not break up or disperse better after applying shear[11] (see Figure S4 for TEM of sheared Sample A), this change in dynamics is associated to the change in entanglements between grafted and matrix chains, and to the free volume available within the aggregated clusters of particles at low graft density.

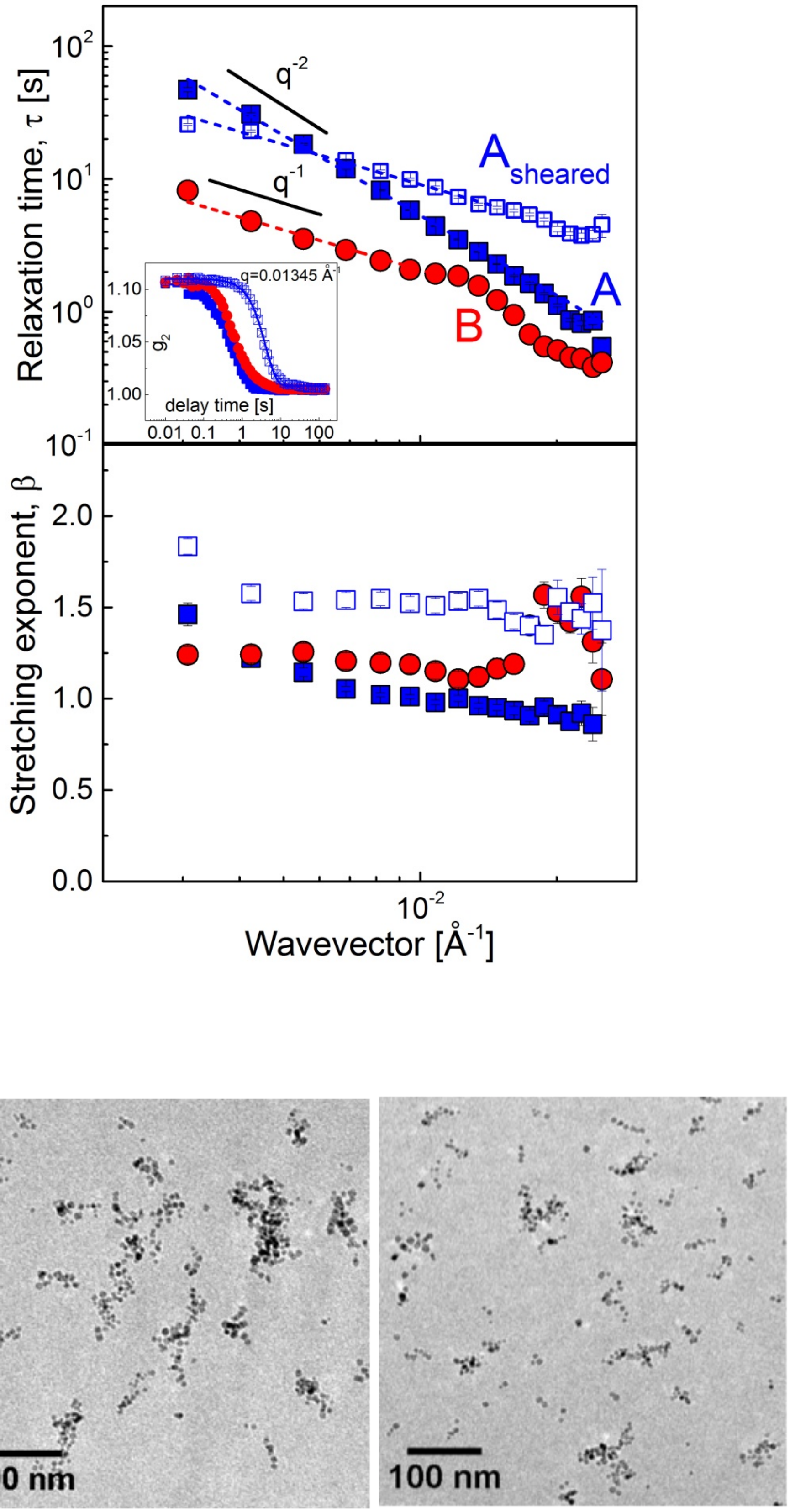
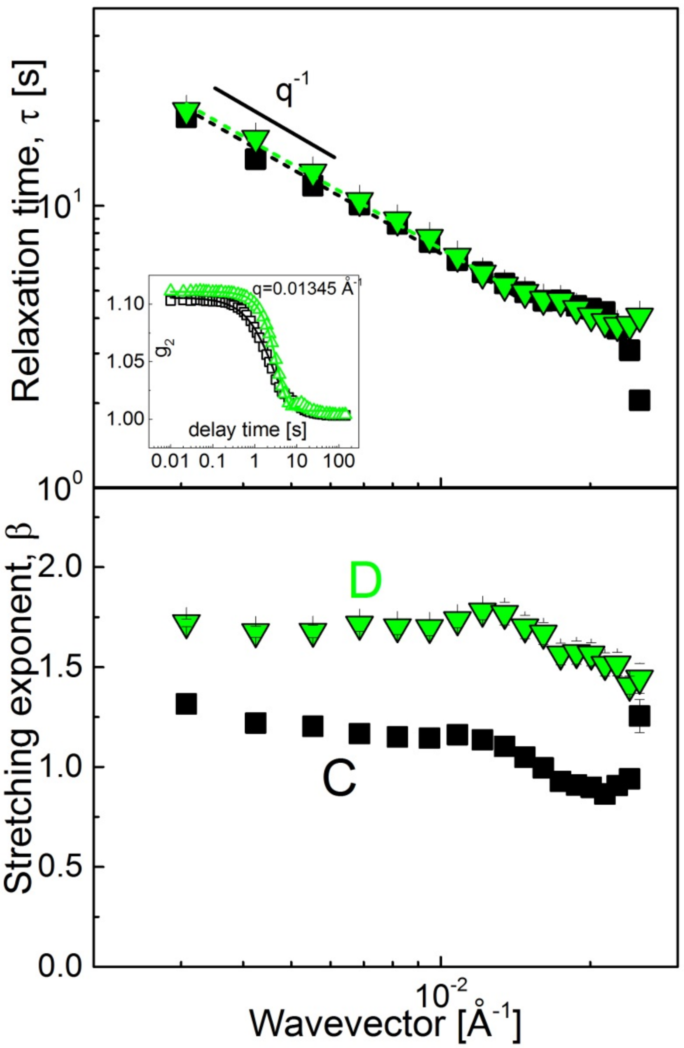


**Figure 1. Effect of matrix chain length on particle relaxations reveals the importance of interface and graft-matrix entanglements on elastic properties.** *Relaxation time (τ) and*

*stretching exponent factor (β) versus q for PS (43 kg/mol)-grafted iron oxide nanoparticles at 0.017 chains/nm$^2$ density. Sample A is for particles in 124 kg/mol PS matrix, and sample B is for particles in 43 kg/mol PS matrix, and sample $A_{sheared}$ is the deformed sample A under oscillatory shear flow at 100% strain. The dashed lines represent power law fits. The inset shows representative intensity autocorrelation functions, $g_2(q,t)$, for each sample at q = 0.01345 Å$^{-1}$. Transmission electron micrograph of sample A (on the left) and sample B (on the right).*

The structured samples C and D both present highly ordered short strings[10,20] with particles moving hyper-diffusively ($\tau \sim q^{-1}$) with similar relaxations (Figure 2). We attribute the origin of this motion to the well entanglement of low graft density brushes with free chains, which was reported and discussed in previous publications on the structural[12], rheological[11] and x-ray/neutron scattering results[10]. Particles in short matrix chains (C) present lower $\beta$ values (< 1.5) than the particles in high matrix chains (D) ($\beta$ = 1.5). We previously showed that strong wetting between low graft density particles and entangled chains creates a highly confined environment around particle structures with an average spacing of ~50 nm, which corresponds to the length of two Gaussian grafted chains that are in contact with each other[20]. In this composite system, where strong interface exists between grafted and free chains, particles behave hyper-diffusively. Contrary to these findings, a previous work has shown that poor wetting and a weak interface could create local stress (called "aging"[21]) and dewetting was speculated to be the main reason for the glassy dynamics in PMMA composites[22]. Another work on particle dynamics in nanocomposites has reported that nanoparticles dilate the entanglement network and lower the composite viscosity, but particle dynamics in entangled polymers did not change and behaved hyper-diffusively[23]. Herein, we present that in structured systems the origin of dynamics is not due to local elastic stress fields, rather it is related to entanglements between grafted particles and matrix chains.


q$^{-1}$
Relaxation time, τ [s]
$10^1$
$10^0$
q=0.01345 Å$^{-1}$
$g_2$
1.10
1.05
1.00
delay time [s]
0.01
0.1
1
10
100
Stretching exponent, β
D
C
2.0
1.5
1.0
0.5
0.0
$10^{-2}$
Wavevector [Å$^{-1}$]

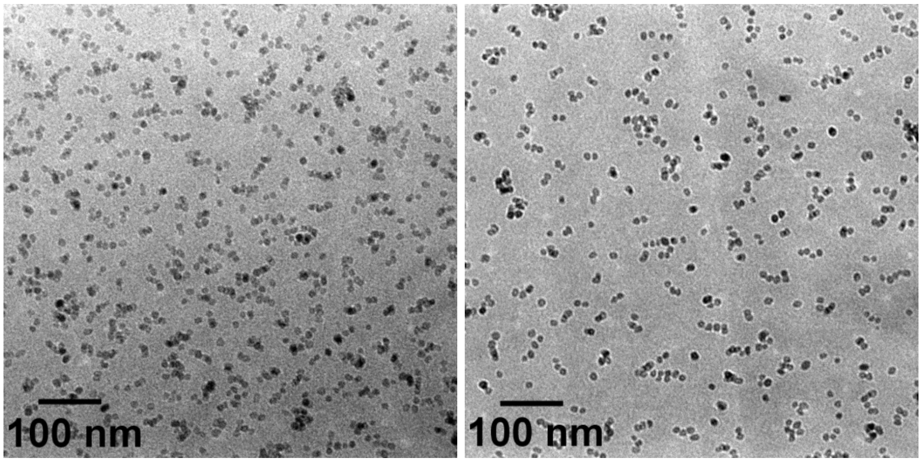

100 nm
100 nm

**Figure 2. Dynamics of string-forming grafted nanoparticles in different molecular weight of matrices.** *Relaxation time (τ) and stretching exponent factor (β) for PS (119 kg/mol)-grafted iron oxide nanoparticles at 0.016 chains/nm$^2$ density. C has the particles in 40.5 kg/mol PS matrix, and D has the particles in 100 kg/mol PS matrix. The inset shows representative intensity autocorrelation functions,* $g_2(q,t)$, *for each sample at* $q = 0.01345$ *Å$^{-1}$. Transmission electron micrograph of sample C (on the left) and sample D (on the right).*

Next, we compared the relaxation times of string forming particles (D) with the well-dispersed case (E) (Figure 3). Samples D and E have grafts of similar length but different graft densities, 0.016 and 0.074 chains/nm$^2$, respectively. The observed structural difference (see Figure 2 for TEM of Sample D and Figure S5 for Sample E) is explained due to strong particle attractions with higher loading and also to the good bridging of particles through matrix-brush entanglements[12]. Relaxation times of particles in a string are found to be smaller than dispersed structure with 15wt% particle loading (Figure 3). Particles both in strings and well-dispersed cases followed heterogeneous hyper-diffusive dynamics with $\beta \approx 1.5$. Thus, comparison of samples with different graft densities (D and E and keeping the other parameters constant), reveals that dynamics mode is more dictated with the strength of interfaces which also governs the dispersion state in grafted particle systems. The hyper-diffusive mode in strings and their faster relaxation suggest that entanglement and particle structures are the factors allowing propagation (or "dissipation") of local stresses through highly correlated string structures.

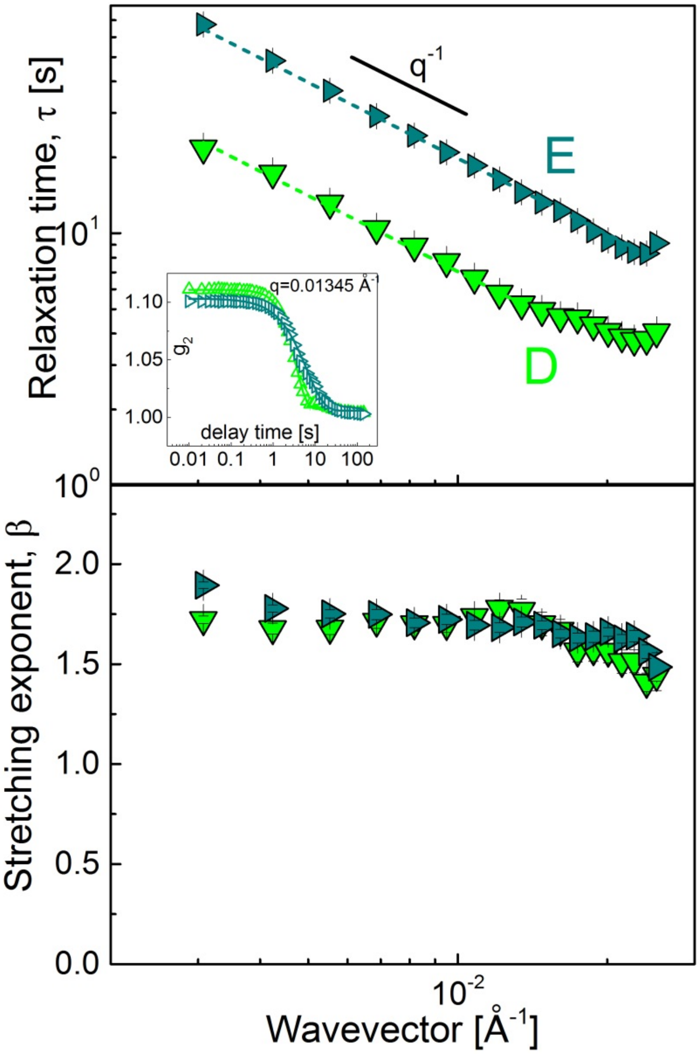
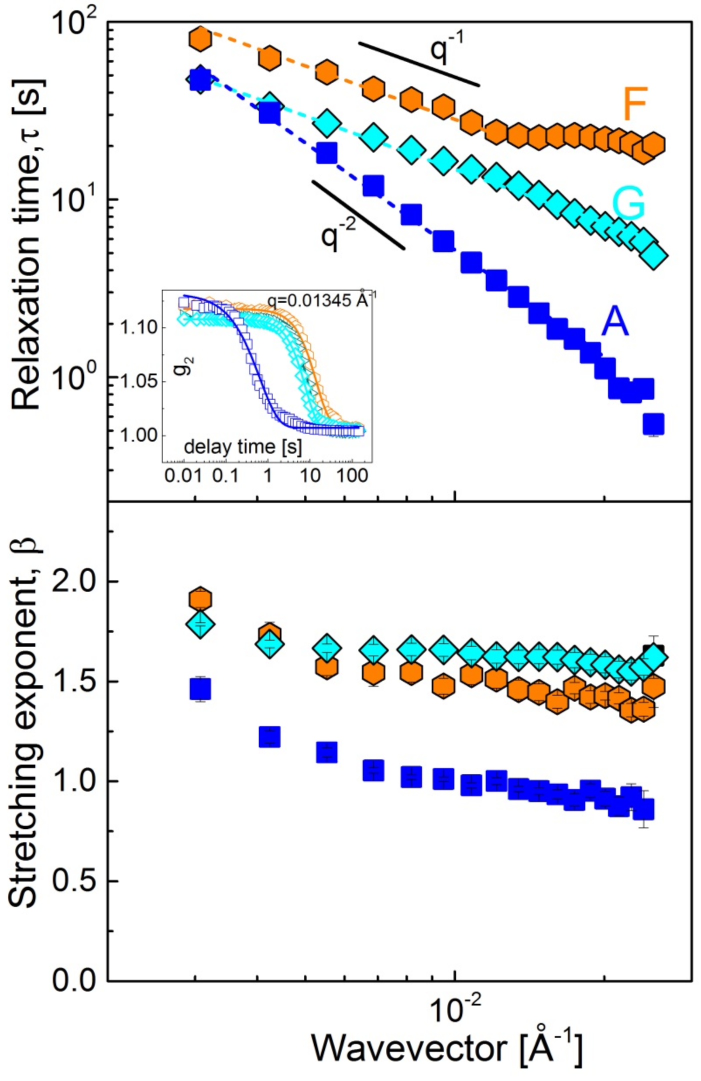


**Figure 3. Comparison of string forming and well-dispersed nanoparticles.** *Relaxation time (τ) and stretching exponent factor (β) of PS (119 kg/mol) grafted iron oxide nanoparticles with different structures. Sample D has the string forming particles with 0.016 chains/nm$^2$ density in 100.2 kg/mol PS matrix, and Sample E has the well-dispersed particles with 0.074 chains/nm$^2$ in 130 kg/mol PS.*

To better understand the particle mobility within different structures, we compared the XPCS data of Samples A, G, F, which have different graft densities but similar matrix molecular weight (≈130 kg/mol). We have shown in prior work (see also Figure 4) that branched structures, spherical aggregates and well-dispersed particles are obtained by slightly changing the graft density in these samples[12]. At the lowest graft density (0.017 chains/nm$^2$), particles behave diffusive. As grafting density increases to 0.057 (G) and 0.12 (F) chains/nm$^2$, particles follow non-diffusive dynamics and their $\beta \approx 1.5$ is consistent with the hyper-diffusive relaxation. It is important to note that samples G and F have higher particle loading, 15 wt%, which creates crowding that may hinder the interface wetting effects on particle mobility. Crowding induced topological constraints have been previously reported for entangled chains and even in short chain systems[24,25].



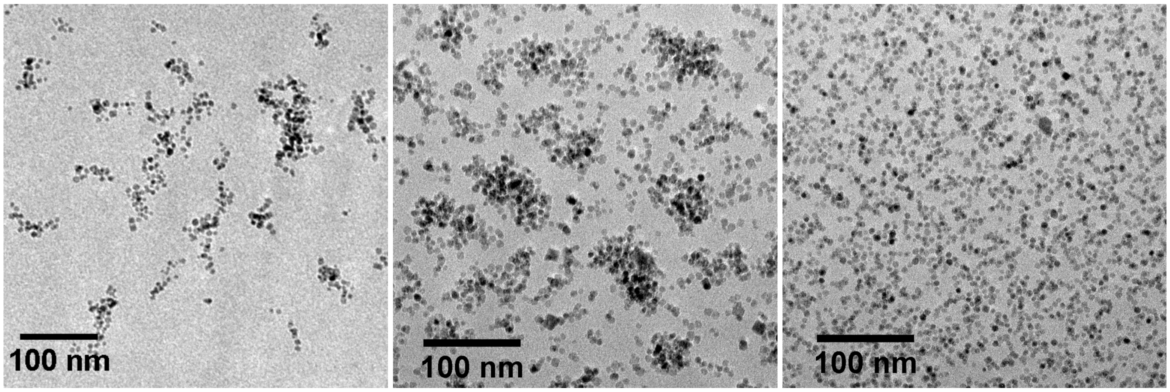


**Figure 4. Particle relaxations within various states of dispersion.** *Relaxation time (τ) and stretching exponent factor (β) versus q for PS (45 kg/mol)-grafted iron oxide nanoparticles at different graft densities in 130 kg/mol PS matrix. Sample A has the particles with 0.017 chains/nm$^2$; sample G has the particles with 0.057 chains/nm$^2$; and sample F has the particles with 0.12 chains/nm$^2$ graft density. Transmission electron micrographs of sample A (on the left), sample G (in the middle) and sample F (on the right). Particle loading is 15 wt% in samples G and F.*

Using composites with similar particle dispersion, which were prepared by mixing low graft density particles with different lengths of free chains, we showed that particle mobility was not directly governed by the organization of nanoparticles, but rather affected by the entanglement of graft-matrix chains and free volume between low density of grafted chains. Particles with short grafts in long matrix chains exhibited diffusive dynamics due to less mixing of grafts with free chains. Upon deformation, the particle dynamics became hyper-diffusive. Particles in strings, spheres or well-dispersed cases followed heterogeneous hyper-diffusive dynamics, which was attributed either to the confined environment of particles for the strings or to the strong wettability of brushes with the matrix. Our findings present the dynamic nature of nanoparticles in different structures of polymer nanocomposites. These results allow us to propose how the free volume between low grafted particles, which is varied with the miscibility of graft and free matrix chains, might be utilized for transport behavior of small molecules in membranes.

## AUTHOR INFORMATION

### Corresponding Author

*Email: pakcora@stevens.edu

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## ASSOCIATED CONTENT

### Supporting Information

Temperature dependence of PS viscosity at different molecular weights; linear viscoelastic master curve; elastic moduli of PS (43 kg/mol)-grafted iron oxide nanoparticles at different grafting densities dispersed in two PS matrices of 43 kg/mol and 124 kg/mol molecular weights; TEM micrograph of sheared Sample A; TEM of Sample E; SAXS data of all the discussed samples.

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Siqi Liu[†], Erkan Senses[†], Yang Jiao[†], Suresh Narayanan[§], and Pinar Akcora[†]

[†]Department of Chemical Engineering and Materials Science

Stevens Institute of Technology, Hoboken, NJ 07030 United States

[§]Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, United States