Supplementary Information for

Nanoparticle-Polymer Interfacial Layer Properties Tunes Fragility and Dynamic Heterogeneity of Athermal Polymer Nanocomposite films

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In the main manuscript, we presented the role of interfacial entropic interaction (characterized by f) in tuning the fragility and the dynamical heterogeneity of polymer nanocomposites. Here, we provide the experimental and simulation details supporting the observations and interpretations discussed in the main manuscript.

1. Sample preparation:

a. Synthesis of PGNPs

Thiol terminated polystyrene grafted gold nanoparticles (PGNP) were synthesized using the *in-situ* grafting-to method as was described by Lennox and coworkers[1]. Thiol terminated polystyrene (PST)and chloroauric acid (HAuCl4.3H2O) were dissolved separately in freshly distilled tetrahydrofuran (THF). The two solutions were then mixed and stirred for *ca*. 20 minutes to ensure homogeneous mixing of the components. Lithium triethylborohydride was added to reduce the chloroauric acid for facilitating the formation of gold nanoparticles. Simultaneously, the PST chains graft to the surface of the growing nanoparticle. Presence of grafted chains on the surface will inhibit further growth of nanoparticles before eventually seizing the growth. These nanoparticles as grown were precipitated by the addition of 3:1 (by volume) mixture of THF and ethanol, which is a good solvent for the free PST chains and a bad solvent

for PGNPs. To ensure a complete removal of the ungrafted PST chains, PGNPs were dissolved in the 3:1 mixture of THF and ethanol and centrifuged. The procedure was repeatedfor4 times [2,3]. Finally, the precipitated PGNPs were dried in a desiccator.

b. Characterization of PGNPs

To determine the overall size of PGNPs, we have performed small angle X-ray scattering measurements on dry powders of PGNPs in transmission geometry. Figure S1 shows the intensity profiles (intensity vs. transmission wave vector) of the two different PGNPs used in this study. A characteristic peak (indicated by an arrow mark in the respective panels) corresponding to the diameter of the PGNPs can be observed. The size of the 3k PST grafted PGNP was determined to be *ca*. 6 nm and that for 20k PS grafted PGNP is around *ca*. 8.5 nm.



Figure **S1**: Intensity profile along the transmission wave vector (q_i) for PGNP with PS grafted molecular weight (a) 3 k Da and (b) 20 k Da is shown. From respective structure factor peaks (indicated by the arrow marks), we have determined the overall diameter of the PGNPs.

The core sizes of the particles were obtained from transmission electron microscopy as shown in figure S2. From this we obtain $R_{Au}^{3k} \approx R_{Au}^{20k} \approx 2$ nm. Here we would like to mention that, considering the polydispersity of the particles and the variation in grafting densities between the two particles used in our studies (*ca.* 25%) implying that the grafting densities of the different particles are not quite different. Consequently, we

anticipate that the minor difference in the grafting densities is not expected to result in any measurable differences in the structure or in the dynamics.



Figure **S2**: *TEM images of PGNPs with graft PST (a) 3 k Da,(b)core size distribution and that of 20 k Da (c and d) provides the estimation of PGNP core diameter. The scale bar shows 50 nm in the TEM images.*

c. Preparation of PNCs

PGNP and PS solutions were made separately and stirred for overnight, before mixing them in appropriate ratios to obtain 0.5% by volume of gold core in the final solution [2, 3]. The estimated total PGNP volume fraction at this core fraction (considering the total size obtained from SAXS) appears to be 2% for 3k PGNP and 6% for 20k PGNP. At this volume fraction, the grafted chain mass fraction in the solution for 3k PGNP becomes 13% and that for 20k PGNP becomes 35%. The mass fractions of matrix chains at this condition are 77% and 56% for 3k and 20k PGNP systems, respectively.

The polymer nanocomposite solutions (PNC) were stirred overnight to ensure a homogeneous distribution of PGNPs. Solutions as obtained were spin coated on a freshly piranha treated silicon substrate. Four

different PNC films were prepared along with bare PS films. Detail of the PNC samples is given in Table S1.

Samples	Mol. Wt of the	Mol. Wt of the	$f = \mathbf{W}_{g} / \mathbf{W}_{m}$	Grafting density
	matrix chains,	grafted chains,		σ
	\mathbf{W}_{m}	\mathbf{W}_{g}		(chains/nm ²)
	(kDa)	(kDa)		
3k50k	50	3	0.06	1.7
20k50k	50	20	0.4	1.3
3k100k	100	3	0.03	1.7
20k100k	100	20	0.2	1.3

Table S1: Important characteristics of the samples used in our studies.

All the films were annealed at a temperature 145° C at a vacuum 10^{-6} mbar for 12 hours to erase possible preparation induced effects.

d. Entropic PNC

In this study, we have used polystyrene as graft as well as matrix chains, hence, there is no enthalpy for mixing. Consequently, the only term that contributes to changes in free energy of the system is entropy, which depends on graft and matrix molecular weights and the grafting density [4]. Therefore, entropy decides the nature of dispersion of the particles and the resultant properties and hence, we called these PNCs as 'entropic PNC'.

2. Dispersion state of PGNPs in annealed films

All the films were imaged using field emission scanning electron microscopy (SEM) to observe the nature of the dispersion state of PGNPs with different *f*. The SEM images of the films are presented in Fig. S3.



Figure S3: Representative SEM micrographs of films with (a) f = 0.03, (b) f = 0.06, (c) f = 0.2 and (d) f = 0.4. A clear improvement in nanoparticle dispersion could be visualized with increase in f.

3. X-ray reflectivity profiles of the films for determining thickness

Thicknesses of the films were obtained from X-ray reflectivity (XR) profiles. The XR profiles of all the films are presented in Fig. S4. Thicknesses of the films were determined from the width of Kiessig-fringes (Δq_z) [2]. The obtained film thicknesses are summarized in the table S2.



Figure S4: XR profiles of PS50 based systems (left panel) and PS100k based systems (right panel) at temperature 403 K.

Sample	Thickness (nm)
PS50k	63.8
f = 0.06	69.5
f = 0.4	70.4
PS100k	73.8
f = 0.03	70.4
f = 0.2	67.6

Table S2: Thickness of the films obtained from XRR at temperature 403K

In order to get the dispersion state of PGNPs along the film thickness, we have modeled [2, 3] the complete XR profiles collected at room temperatures before performing XPCS and the extracted electron density profiles are shown in the Fig. S5.



Figure S5: Electron density profiles along the perpendicular direction of the film surface extracted by modeling XR profiles [3] showing the dispersion state of the PGNPs.

We can see from the figure that the PNC films with smaller f show a preferential segregation to the surface and interface, which is in accordance with our earlier reports [2]. However, since we used relatively smaller fractions of the particles, the extent of segregation is smaller. These electron density profiles only provide the

state of dispersion of particles at room temperature. However, at higher temperatures where the XPCS experiments are performed, the extent of dispersion will enhance as we have shown in [3]. Given this minimal segregation, we do not expect the dynamics measured at high temperature to be significantly influenced by the dispersion state of PGNPs in the films.

4. X-ray photon correlation spectroscopy and analysis:



A typical CCD image collected during XPCS measurements is shown in Fig. S6 [5].

Figure S6: A typical CCD image collected on PS100k sample in the reflection geometry at an incident angle, 0.15°, lesser than the film critical angle 0.16°.

are shown in Fig S7.



Figure S7: Typical two time correlation functions for samples (from left) 3k50k, 3k100k and 20k100k.

The plots of the current systems show no variation in intensity with time (along the diagonal of the plot) indicating no time evolution of the system during measurements [6,7]. The samples therefore are in equilibrium.

The $F(q_x, t)$ obtained from XPCS measurements are shown in Fig. S8 for all the samples at different temperatures for a particular q_x .



Figure **S8**: *ISF* for (a) bare PS50k, (b) f = 0.06, (c) f = 0.4, (d) PS100k, (e) f = 0.03, and (f) f = 0.2 as a function of t at different temperatures along with the fits (red solid lines).

Extracted relaxation rate $\Gamma(q_x)$ for the PS100k based samples are shown in Fig. S9, as a function of $q_x h$.



Figure **S9**: Relaxation rate (Γ) as a function of $q_x h$ at different temperatures for PS100k (a), for f = 0.03 (b) and that for f = 0.2.



Figure S10: Comparison of surface and bulk relaxation times as a function of q_x for sample a) 3k50k and b) 20k50k. XRR data along with the fits (red curves) for adsorbed layer obtained after rinsing with toluene.

In the figure S10 a) and b), we have shown the comparison of surface and bulk relaxation for sample 3k50k and 20k50k respectively. As can be seen, (a) the q_x - dependence of the relaxation time is similar for both surface and bulk mode, indicating that we measure the relaxation of capillary waves on the surface, and (b) we do not observe significant changes in surface and bulk mode of dynamics in case of 3k50k, while 20k50k exhibits a slightly faster dynamics at the surface. Since the q_x -dependence is similar and the relaxation times are similar (even for 20k50k PNC the variation is only a factor of 2-3), we believe that the temperature dependence of viscosity and therefore, the fragility values would not change irrespective of whether we use surface or the bulk measurement. We have also measured the thickness of adsorbed layer of these films after washing-off the surf and bulk part of the film with toluene. Measured thickness of adsorbed layer for 20k50k sample is ~1.7 nm and that for 3k50k sample is ~3.3 nm respectively. XRR fits for adsorbed layer along with the fits using parratt's formalism is given in figure S10 c).

5. VFT modeling to the viscosity of the films:

The estimated viscosity (presented in main manuscript) indicates temperature dependence described by Vogel-Fulcher-Tammann (VFT) equation given by

$$\eta = \eta_0 e^{\frac{BT_0}{T - T_0}}....(2)$$

Using this equation, the viscosity was modeled and the fit was extrapolated till $T = T_g$. The Vogel-Fulcher temperature, T_0 was estimated from the glass transition temperature using the relation, $T_0 = T_g - 50$. These estimated values of T_0 were used to fit the experimental data with eqn 2. The details of T_g measurements are given in the next section. VFT fit for PS50k, extrapolated till $T = T_g$, is shown in Fig. S11. From such VFT fits, we have extracted the fragility, *m*, given by

$$m = \frac{\partial \log \eta}{\partial (\frac{Tg}{T})} |_{T_g}....(3)$$

The slope of the η vs T plot near T_g was used to determine m, which are summarized in Fig. 5 (a) of the main manuscript.

In order to estimate errors in *m*, we have varied the value of parameter T_0 according to the error bars in experimentally estimated T_g . Corresponding VFT fits provide the extreme values of the fragility, which gives the estimate of errors in *m*. A typical plot showing the three fits for sample PS50k, where T_g is varied within its error bar is shown in Fig. S11. This provides a larger error in *m*. We also include the errors obtained in the fit parameters, e.g. *B* in equation 2. This is how the errors are calculated and plotted in Fig. 5 (a) of the main manuscript.



Figure **S11**: Figure shows VFT fit (red dashed line) to the viscosity of PS50K sample and the extrapolation of the VFT fit from which the slope near $T_g(T/T_g = 1)$ is calculated to determine the fragility, m. The green lines show the fits at two extreme values of $T_g(T_g$ -error bar and T_g +error bar) which provides the actual error in estimating m.



Figure S12: Temperature dependent F-D retrace curve for PS film of thickness 65nm. Red curve on the T=423K data shows the slope on the retrace curve.

Conventional T_g measurements for bulk PNCs, such as differential scanning calorimetry (DSC) cannot be performed on these PNC films. Hence, T_g was measured using atomic force microscope based forcedistance spectroscopy measurements performed at different temperatures [2,8]. We used a SiO₂cantileverwith a curvature of tip radius ~10 nm and resonance frequency ~150kHz. Force experienced by the tip due to tip-sample interaction was recorded from the cantilever deflection as a function of tip-sample distance. The change in slope of the retrace curve was observed with increasing temperature (Fig. S12) as observed earlier [2]. The slope gives a measure of the combined stiffness of sample and cantilever. This slope has been plotted as a function of temperature in Fig. S13. The transition temperature can be estimated by modeling the data with a sigmoidal function and extracting the inflection point. All the calculated T_g values are summarized in a table (see Table S3).



Figure **S13**: Slope of retrace curves as a function of temperature for all PS50k based samples (top panels) and PS100k based samples (bottom panels) showing the variation of T_g with f compared to bare PS films.

Samples	f	Т _g (К)
PS50k	0	377 ± 3
3k50k	0.06	376 ± 4
20k50k	0.4	379 ± 5
PS100k	0	378 ± 3
3k100k	0.03	362 ± 3
20k100k	0.2	375±4

Table S3: Estimated T_g values using AFM force-distance spectroscopy

In order to estimate error bars in T_g we have used the following method. The *F/d* data was fitted with a sigmoidal equation to find the inflection point. Then, we have manually fitted the data with the extreme values (blue curve for the lower extreme and green curve for the higher extreme in Fig. S14) that could fit the data without considerably affecting the χ^2 values. We use the average of the extreme values as the mean T_g and the deviation as error bar (refer the table S3).



Figure S14: *F/d data with fits showing the possible range of* T_g *providing the estimation of error bars in* T_g for sample PS50k (left panel) and 3k50k (right panel)

Using AFM based force distance spectroscopy for measuring T_g has been established earlier by ourselves and others [2, 8, 9, 10]. It has been shown that this approach gives reliable T_g values, which can be compared with other conventional techniques like DSC (in bulk) and ellipsometry (in thin films). For example, as shown in Fig. S13, within the experimental error, T_g values of polystyrene films composed of $M_w = 100$ kg/mol and $M_w = 50$ kg/mol, yield values that are in good agreement with the bulk values obtained by DSC [11]. We have shown a comparison of T_g estimated from DSC on bulk PNC and AFM on films in table S4. Our result suggests that they are as accurate as DSC, reaffirming that AFM based experiments are one of the most reliable techniques for measuring T_g on such films. Moreover, the accuracy obtained in T_g determination is sufficient for fragility estimation which is the primary purpose of T_g measurements in this manuscript.

Samples	AFM T _g	DSC $T_{\rm g}$
	(K)	(K)
PS100k	378	378
PS50k	377	376
20k100k	375	376

Table S4: Comparison of T_g values estimated from DSC and AFM

20k50k	379	375

7. Calculation of viscosity and fragility from MD simulation:

The model nanocomposites were prepared by generating a mixture of amorphous linear polymer chains and polymer-grafted nanoparticles (PGNP) in a cubical simulation box with periodic boundary conditions on all three sides. The matrix and grafted polymers were modeled as coarse-grained bead-spring chains, using the finite extensible nonlinear elastic potential with standard values [12]. All monomers were chemically identical with reduced mass M=1.0 and diameter $\sigma=1$. The degree of polymerization for the matrix chains was fixed at $M_m = 50$, while the graft length Mg was varied from 3 to 20 such that the ratio f $= M_g/M_m$ varied from 0.06 to 0.4. The nanoparticles were represented as uniform spheres of size D = 4σ and mass proportional to D^3 . Polymer-grafted nanoparticles were then constructed by uniformly grafting polymer chains onto the surface of each nanoparticle such that the grafting density is $\sigma_g = 0.7/\sigma^2$. A typical snapshot of one such system is shown in Fig. S15.



Figure S15: Visual Molecular Dynamics (VMD) [19] Snap shot of a typical composite system. Nanoparticle (Blue), Tethered (Red), Grafted(Purple), Matrix monomers (Green). The graft chain here hasN=3monomers. The density of matrix is reduced than actual value to show different components.

The number of polymer chains (N_m) and nanoparticles (N_n) in the system were chosen such that the volume fraction of nanoparticles is $\varphi_n = D^3 N_n / (d^3 N_m + D^3 N_n) = 0.05$. The initial configurations were generated by randomly placing all particles within the box and any overlaps between monomers are removed by applying a soft cosine potential that slowly pushes the particles apart until the distance between their centers is equal to sum of the two radii [12]. The core and tethered beads of PGNP were treated as a single rigid body to prevent sliding of grafted chains on the particle surface. The pair-wise interactions between all monomers in the system were defined using a shifted Lennard-Jones (LJ) potential of the form [12]

$$E = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] - E_{r_c} \qquad (4)$$

truncated at $r_c = 2.5\sigma$, where σ is the monomer size, ε is the energy scale, and E_{r_c} is the potential at the cutoff distance r_c . The polymer-nanoparticle interaction was the LJ potential with a cutoff distance $r_c = D/2 + \sigma$, while two nanoparticles interacted with apurely repulsive LJ interaction. All thermodynamic quantities are expressed in reduced units are convenient in molecular simulations. The systems were equilibrated by running isobarically at $P^*=0$ that represents atmospheric pressure [14], and then at constant volumeuntil the chains move their own size using the LAMMPS simulation package [15]. The desired temperature was maintained using a Nose-Hoover thermostat with a damping parameter of 0.1. The specific volume of the system as a function of temperature to estimate Tg was collected from subsequent production runs. The viscosity of the composite was estimated following two procedures at different temperatures. At high temperatures ($T/T_g > 1.55$), the zero shear rate viscosity was calculated from the stress autocorrelation function using the Green-Kubo relation [16],

$$\eta = \frac{V}{k_B T} \int_0^\infty \langle \sigma(t) \sigma(0) \rangle dt....(5)$$

Where *V* is the volume, *T* is the temperature, and k_B is the Boltzmann's constant. At lower temperatures $(T/T_g \le 1.55)$, the SLLOD equations of motion, which adopts the transpose of the qp-DOLLS tensor [17] were integrated at a strain rate $\dot{\gamma}$ using a timestep of $\delta t = 0.005\tau$, where $\tau = \sqrt{(M\sigma^2/\varepsilon)}$, and M is the mass of a chain monomer, such that the diagonal components of the pressure tensor equal to zero [18]. The shear viscosity is calculated using $\eta = \langle P_{xz} \rangle / \dot{\gamma}$, where $\langle P_{xz} \rangle$ is the xz component of the pressuretensor along the flow and gradient directions, respectively. The viscosity values obtained from the two temperature ranges using two different methods have been merged to get a larger range of temperature. All results reported here are obtained by averaging valuesfrom three independent simulations. Calculated viscosities with varying temperature are shown in Fig. S16.



Figure **S16**: *Figure shows viscosity calculated as a function of temperature for neat polymer (red solid symbol) and different f values as labeled in the figure.*

The temperature dependent viscosity was fitted with VFT equation keeping the parameter $log(\eta_0)$ fix at a particular value (0.534 obtained from pure polymer data fitting) to reduce the number of fit parameters. Fragility of these systemswere calculated using this method and summarized in Fig 5(b) of main manuscript.

8. Calculation of diffusion coefficient:

a. System details:

The polymer and polymer grafted nanoparticles were modeled as described in previous section. However, in this case we have just a single PGNP fixed at the center of simulation box. In order to study systems with different $f\left(=\frac{N_{grafted}}{N_{matrix}}\right)$, we varied the number of monomer units of the grafted chains while keeping the matrix chain length fixed at N = 300. So, for higher *f* values we have a larger PGNP. Therefore, in order to have a well-defined bulk and interfacial region, the number of matrix chains was made higher for larger *f* systems. We have 600, 350 and 200 matrix polymer chains for f = 0.13, 0.06 and 0.03 respectively which are summarized in table S5. Figure S17 shows a snapshot of one such system with lesser density than actual value.

Table S5 :	System	details
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System	Grafted chain length	Matrix chain length	f
1	10	300	0.03
2	18	300	0.06
3	40	300	0.13



Figure S17: VMD [19] snapshot for f = 0.06 system. The Nanoparticle (blue), Grafted chains (Pink) matrix chain monomers (Green). The graft chain here has N=18 monomers. In this figure, the density of matrix as well as graft is reduced than actual value to show different components clearly.

b. Equilibration

The systems were equilibrated at constant volume and temperature $1\epsilon/k$. The thermostat and damping parameter issame as described in previous section. The equilibration is achieved by running each simulation for $1.5*10^6$ or 300 million MD time steps each time steps being 0.005τ . The equilibration is checked by calculating the mean square internal displacement (MSID) [20]. The saturation of MSID is taken as signature of equilibration. MSID is shown in Fig. S18.



Figure **S18**: *MSID for matrix chains. Saturation of MSID was taken to be the signature of equilibration* [15].

c. Radial density of grafted monomers

The interfacial region is defined as the region lying within a radial distance of $r \sim R_n + h_g + R_g/2$, where, R_n , h_g and R_g are the radius of PGNP core, brush height of grafted chains and the radius of gyration of matrix polymers respectively. The brush height h_g is defined as [21,22],

where, $\rho(r)$ is the radial density of grafted monomers. The bulk and interfacial regions are shown in the density profiles (Fig. S19) of matrix and graft monomers.



Figure **S19**: Radial density profiles for graft monomers (open symbols) and Matrix monomers (solid symbols) showing bulk and interfacial region. The right side region of the vertical dashed line corresponds to bulk and the left side corresponds to interfacial region. The dashed lines are coloured such that a dashed line of particular colour represents interface boundary for a density profile with that colour.

d. Penetration depth, λ

Penetration of matrix chains into the graft polymer brushes were quantified using the parameter, penetration depth, λ , given by

where $\rho_m(r)$ is the is the matrix radial density profile from the center of nanoparticle, r is the radial distance, Rn is the radius of nanoparticle and h_g is the graft chain brush height.



Figure S20: Penetration depth calculated for different f's.

9. Diffusivity calculation

The equilibrated systems are run for further 300 million time steps ($\Delta t = 0.005$) in order to calculate the diffusivity. The MSD of center of mass is given by [13],

$$g_3(t) = \langle [r_{cm}(t_2) - r_{cm}(t_1)]^2 \rangle \dots (8)$$

where $r_{cm}(t)$ is the center of mass position at time t and (.) denotes time and ensemble averaging. The diffusivity is calculated using Einstein's equation,

 $g_3(t) = 6Dt \dots (9)$

For a given system, we calculated the MSD (Fig. S21) for two different regions, interfacial and bulk region, in the simulation box. The values of diffusivity at interface and bulk regimesare summarized in table S6.



Figure **S21**: *MSD for different systems*. (A) *f*=0.03 (B) *f*=0.06 and (C) *f*=0.13.

Table S6:	Diffusivity	values
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<i>f</i> -values	Interface diffusivity $(x \frac{10^{-4}}{6} \sigma^2 / \tau)$	Interface diffusivity $(x\frac{10^{-4}}{6}\sigma^2/\tau)$
0.03	2.65	2.47
0.06	2.24	2.17
0.13	2.33	2.47

10. Calculation of Tg of the simulation systems:

For the calculation of fragility, T_g is estimated from the temperature dependence of specific volume. It is calculated as the point at which the slope of the specific volume vs temperature curve changes. One typical plot showing T_g of the system is shown in Fig. S22.



Fig. S22: Variation of specific volume for a bulk polystyrene ($Mw \sim 50$ kDa) system generated using coarse grained molecular dynamics simulation. The point at which slope change occurs is taken as Tg.

11. Non-Gaussian parameter

The Non-Gaussian parameter was calculated using [23],

$$\alpha_2(t) = \frac{3\langle \Delta r(t)^4 \rangle}{5\langle \Delta r(t)^2 \rangle^2} - 1....(10)$$

Where $\langle . \rangle$ denotes time and ensemble averaging over all the monomers in the system. $\Delta r(t)$ is the displacement of a monomer in a time interval *t*. The NGP for all the system is shown in Fig. S23. The peak value of α_2 , that characterizes the microscopic dynamics of the system, is summarized in Fig. 6(a) in the main manuscript.



Figure S23: Non-Gaussian parameter for different systems

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