# Supplementary information for Viscosity and Fragility of Confined Polymer Nanocomposites: A Tale of Two Interfaces

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Complementing the main text, "Viscosity and Fragility of Confined Polymer Nanocomposites: A Tale of Two Interfaces" here we include details of the sample preparation, analysis of dispersion of particles, deducing relaxation times, viscosities, and fragilities. Also included are the details of simulation methods and the associated analysis.

# 1. Sample preparation:

### I. Synthesize of PGNPs

Polystyrene grafted gold nanoparticles (PGNPs) are synthesized by following a graftingto method.<sup>1,2</sup> Two types of PGNPs with different molecular weights for graft polymers viz.  $M_g = 3 \ kDa$  and 20 kDa are synthesized. Thiol-terminated polystyrene (PST) is dissolved and stirred overnight in distilled tetrahydrofuran (THF). Gold(III) chloride trihydrate (HAuCl<sub>4</sub>.3H<sub>2</sub>O) is dissolved separately in THF is mixed with PST solution and kept stirring for 30 minutes in ice bath. A reducing agent superhydride is added to this mixture drop by drop, which leads to the reduction of gold ions and formation of Au nanoparticles (NPs) with simultaneous grafting of PST chains eventually resulting in the formation of polystyrene grafted nanoparticles. After stirring the solution for 90 minutes, a few milliliters of ethanol is added to terminate the chemical reaction. Addition of ethanol selectively precipitates grafted PST chains. PGNPs settle down during centrifugation and supernatant liquid with ungrafted chains is disposed. Ungrafted polymer chains are completely removed by following this selective precipitation procedure 4-5 times. Finally, the precipitated PGNPs are dissolved in THF and vacuum dried for 2-3 hours.

#### **II.** Characterization of PGNPs

PGNPs are characterized using Transmission electron microscopy (TEM), Small angle X-ray Scattering (SAXS) and Thermo gravimetric analysis (TGA). The size of nanoparticle cores for PGNP3k and PGNP20k are obtained from TEM images which are in Figure S1. Inset of Figure S1 shows Au core size distribution. Total size of the PGNPs are determined from SAXS measurements (Bruker Nanostar, USA) with an incident X-ray of wavelength of 1.54. Weight fraction of Au core in PGNPs are calculated from TGA (Figure S1d). Table S1 summarizes the different characteristics of both PGNP3k and PGNP20k.

Sample	$M_{\rm g}$	radius of Au core	grafting density	radius of PGNP
	(kDa)	(nm)	$\rm chains/nm^2$	(nm)
PGNP3k	3	$1.66\pm0.5$	2.4	3.05
PGNP20k	20	$1.67\pm0.5$	1.0	5.4

Table S1: Specification of PGNPs



Figure S1: TEM images of PGNPs with graft of a)  $M_g = 3 \ kDa$  and b)  $M_g = 20 \ kDa$ , scale bar is 20 nm. Inset gives size distribution of Au core. c) SAXS profile and c) TGA data of both particles.

#### III. Preparation of PNC thin films

PS and PGNPs are dissolved in toluene separately and stirred overnight. After overnight sirring, PS and PGNP solutions are mixed in a certain ratio to get the final volume fraction of gold in PNC solution as 0.5%. Polymer nanocomposite solutions are stirred overnight to ensure homogeneous mixing. Thin films of PNCs are made by spin coating PNC solutions on a pirahna treated 15 x 15 mm<sup>2</sup> silicon substrate. Different thicknesses of PNC films viz. 65 nm, 50 nm, 40 nm and 30 nm are prepared. Thin films are annealed at 145 °C (well above  $T_g$  (/sim 100 °C) for PS) in vacuum of 5 ×10<sup>-5</sup> mbar for 12 hours.

# 2. Lateral dispersion of PGNPs from FESEM

Thin films are imaged using field emission scanning electron microscopy (FESEM) with voltage 5 kV. Lateral disperion of PGNPs could be visualized from SEM images (Figure S2a to g).



Figure S2: SEM micrographs of annealed samples. a) to c) 65 nm , 40 nm, and 30 nm films of PNC-S. d) to g) 65 nm , 40 nm, 50 nm and 30 nm films of PNC-L. Scale bars are of length 200 nm.

#### 3. Determination of surface segregation of PGNPs from XR

X-ray reflectivity (XR) technique is used to characterize the dispersion of PGNPs along the thickness of the films. XR data is collected using Rigaku SmartLab Xray Diffractometer with incident wavelength of  $\lambda = 1.54$  Å and at Photon Factory, Japan with incident wavelength of  $\lambda = 1.12$  Å. XR data is modeled using parratt's formalism with three layers model (surface, bulk and interface), as shown in Figure S3a. Red curves in Figure S3b and S3c shows best fit to the data. The extracted electron density profiles are shown in Figure S4. Volume fractions of Au at each layers are extracted from the electron density ( $\rho$ ) using the following formula,

$$\phi_{layer} = \frac{\rho_{layer} - \rho_{PS}}{\rho_{Au} - \rho_{PS}} \frac{h_{layer}}{h_{total}},$$
(1)

### 4. Adsorbed layer thickness

Adsorbed layer thickness of the films are measured by washing the top surface of thin films with toluene. Thickness of the washed films are measured using XRR. XRR data along with the fits are given in Fig. S5. It is clear that the adsorbed layer thickness increases with decreasing film thickness.

## 5. Study of dynamics using XPCS

X-ray photon correlation spectroscopy (XPCS) measurements on annealed PNC and pure PS films give information of dynamical aspects of thin films. Incident X-ray beam of energy 8 keV with size 25 x 25  $\mu$ m<sup>2</sup> is used to probe the dynamics. Time dependent scattered intensity was collected using Lambda detector (area 1536 x 512 px<sup>2</sup> (84.5 x 28.2 mm<sup>2</sup>), pixel size of 55 x 55  $\mu$ m<sup>2</sup>).<sup>3,4</sup> Scattering intensity is divided into 12-18 q<sub>x</sub>-partitions and the average intensity from these partitions  $I(q_x, t)$  is taken to calculate auto correlation calculation. Auto correlation extraction from scattering data is performed using a MATLAB based graphical user interface (XPCSGUI) developed



Figure S3: Three layer model used for XR data modeling. X-ray reflectivity profiles of b) PNC-S and c) PNC-L films. Curves are shifted for clarity. Red curves represent fits to XR profiles using parratt's recursion formalism.



Figure S4: The electron density profiles of a) PNC-S and b) PNC-L films extracted from the XR profiles shown in Figure S3.



Figure S5: XR data and fits (red curve) of washed films of a) PS, b) PNC-S and c) PNC-L.



Figure S6: The electron density profiles of washed a) PNC-S and b) PNC-L films extracted from the XR profiles shown in Figure S5.

by P10 (Petra III, DESY, Germany) beamline scientists. Intensity autocorrelation function is given by

$$g_2(q_{\mathbf{x}}, t) = \frac{\langle I(q_{\mathbf{x}}, t) \rangle \langle I(q_{\mathbf{x}}, t + \delta t) \rangle}{|I(q_{\mathbf{x}}, t)|^2},\tag{2}$$

Intermediate scattering function (ISF),  $f(q_x, t)$  is related to  $g_2(q_x, t)$  by the following relation,

$$g_2(q_{\mathbf{x}},t) = 1 + b |f(q_{\mathbf{x}},t)^2|, \qquad (3)$$

where b is an instrumental factor called the speckle contrast and t is delay time. ISFs of all samples at  $q_{\rm x} \approx 0.00086^{-1}$  is given in Figure S7.  $f(q_{\rm x}, t)$  has the general time dependent functional form,

$$f(q_{\mathbf{x}},t) = exp\left[-\left(t/\tau\right)^{\beta}\right],\tag{4}$$

where  $\tau$  and  $\beta$  are the relaxation time and Kohlrausch exponent, respectively. The normalized relaxation rate  $\Gamma h$  for all samples is given in Figure S8.

The normalized relaxation rate  $\Gamma h$  as a function of  $q_{\rm x}h$  was fitted with a general



Figure S7: ISFs of a) PS b) PNC-S c) PNC-L at temperature T = 423 K, Red curves represents the fits using equation 4.

viscoelastic-capillary wave equation,  $^5$ 

$$\Gamma h = \frac{\gamma}{2\eta} \frac{q_{\rm x} h \left[ \sinh(q_{\rm x} h) \cosh(q_{\rm x} h) - q_{\rm x} h \right]}{\cosh^2(q_{\rm x} h) + (q_{\rm x} h)^2} + h \left(\frac{\mu}{\eta}\right) \tag{5}$$

where  $\eta$ ,  $\mu$  and  $\gamma$  are viscosity, elastic modulus and surface tension of film, respectively. In most cases, viscous-capillary wave equation ( $\mu = 0$ ) fitted the data well except for low temperature data (T = 403 K and 413 K) of 30 nm films of PNC samples. Figure S9b shows comparison of viscous-capillary and viscoelastic-capillary fits to normalized relaxation rate of PNC-S 30 nm data at T = 413 K. In this case, viscoelastic-capillary model gives better fit to the data as compared to viscous-capillary model.

# 6. Modeling temperature dependence of viscosity using VFT equations

Temperature variation of viscosity is modelled with Vogel-Fulcher-Tammann (VFT) equation,<sup>6</sup>

$$\eta = \eta_{\rm o} \exp\left(\frac{BT_{\rm o}}{T - T_{\rm o}}\right). \tag{6}$$

where  $\eta_{\rm o}$  and B are the fit parameters and  $T_{\rm o}$  is called Vogel temperature. Since



Figure S8: Normalized relaxation rates at different temperatures for pure PS films of thickness a) 65 nm b) 40 nm and c) 30 nm; for PNC-S films of thickness d) 65 nm e) 40 nm and f) 30 nm; PNC-L films of thickness g) 65 nm h) 50 nm (closed symbols) and 40 nm (open symbols) and i) 30 nm.



Figure S9: a) Normalized relaxation rate for pure PS50k (h = 40 nm) film as a function of  $q_x h$  at T = 423 K. Red curve represent fit to viscous-capillary model. b) Normalized relaxation rate for PNC-S 30 nm film as a function of  $q_x h$  at T = 413 K. Red and green curve represent fit to viscoelastic and viscous-capillary model respectively. In this case viscoelastic-capillary model fits the data better than viscous-capillary model.

there are three unknown parameters in the VFT equation, to reduce uncertainty in the fits, we have approximated  $T_o = T_g - 50K$  based on earlier reports.<sup>7–9</sup>  $T_g$  values are measured using AFM F-D spectroscopy as discussed in the earlier reports,<sup>2,4</sup> and given in Table S2. Sigmoidal fits to the temperature dependence of the slopes of retrace curves for all the samples are shown in Figure S10. The change in  $T_g$  with respect to pristine PS films as a function of film thickness is shown in Figure S11.

VFT modeling of viscosity data is depicted in Figure S12. Red curve is the VFT fit to the data. Fit is extrapolated to  $T = T_{\rm g}$  and slope of the curve at  $\frac{T_{\rm g}}{T} = 1$  gives fragility (Fig 6). Mathematically, fragility (m) is given by,

$$m = \frac{\partial ln\eta}{\partial \left(\frac{T_{\rm g}}{T}\right)}\Big|_{T_{\rm g}}.$$
(7)



Figure S10:  $T_{\rm g}$  determination using AFM F-D. slope of retrace FD spectroscopy curves vs temperature (Black open squares) and sigmoidal fit to the data (red curve). Each row represents data for PS, PNC-S and PNC-L samples.

Sample	Thickness	Glass transition temperature
	(nm)	(K)
$\mathbf{PS}$	65	$377 \pm 3$
	40	$367 \pm 2$
	30	$367 \pm 1$
PNC-S	65	$376 \pm 1$
	40	$362 \pm 4$
	30	$360 \pm 5$
PNC-L	65	$379 \pm 5$
	50	$366 \pm 3$
	40	$369 \pm 2$
	30	$362 \pm 2$

Table S2: Glass transition temperature of samples



Figure S11: The changes in PNC  $T_g$  with respect to the pristine PS films  $T_g$  ( $\Delta T_g = T_g(PNC) - T_g(PS)$ ), of respective, thickness, are shown as a function of film thickness for both the PNCs. The  $T_g$  values are generally higher for higher f films which seems to correlate with  $\eta$  variation. However, the dependence on  $h_{int}$  is not very consistent. While it scales very well for intermediate thickness PNC-L films such correlations are not observed for other samples.



Figure S12: Temperature dependence of viscosity of a) PNC-L b) PNC-S samples of thickness 30 nm. Dotted lines represents multiple VFT fits (and extrapolation to  $T = T_{\rm g}$ ) which are passing through data points within error bars.



Figure S13: Comparison of viscosity of PNC-L with two different interface thicknesses with that of PS.

#### Error in fragility calculation

Error in the determination of fragility values of these systems are calculated by fitting multiple VFT curves through the data points (Figure S12). For this purpose, the fit parameters B and  $T_{\rm o}$  are varied.  $T_{\rm o}$  is varied within error bars of  $T_{\rm g}$ . Standard deviation of fragility values extracted from all three fits are taken as the error in fragility due to extrapolation.<sup>4</sup> This method is used for all the films and are shown in Fig. 6a of the main manuscript.

#### Surface and Bulk modes

To establish the effect of adsorbed layer on surface dynamics of PNCs, we have extracted surface and bulk viscosity of PNC-L using XPCS-surface and bulk mode scattering. Figure S13 shows the change in viscosity of two PNC-L films with two different adsorbed layer thicknesses. There is a clear increase in bulk viscosity for PNC-L (h =40 nm) system as compared to surface viscosity, which is induced by the presence of thick adsorbed layer.

## 7. MD simulation

#### Structure and density profile

To get more insight into the experimental observations, we performed coarse grained molecular dynamic simulations. The system here consists of a mixture of linear chain grafted nanoparticles and free linear chains in a cuboid simulation box with periodic boundary conditions along Y and Z-direction. The system is confined along X-direction using two rigid walls. The linear chains are generated using bead-spring model with finite extensible nonlinear elastic potential with standard values of the parameters.<sup>10</sup> The system consists of identical monomers with diameter 1  $\sigma$  and reduced mass M = 1. Number of monomers in matrix chain is kept constant ( $N_{\rm m} = 40$ ) and two different types of grafts are used by varying number of monomers in graft chain ( $N_{\rm g} = 3$ , 15), hence there are two f values ( $f = N_{\rm g}/N_{\rm m} = 0.075, 0.375$ ). Nanoparticles are modeled as uniform spheres of diameter D = 4  $\sigma$ . Graft chains are uniformly attached to the surface of NPs to make PGNPs. 20 chains are attached to a single NP. Volume fraction of NPs in the system is kept constant ( $\phi_{\rm NP} = \frac{D^3 N_{\rm NP}}{(d^3 N_{\rm m} N_{\rm p} + D^3 N_{\rm NP})} = 0.05$ , where  $N_{\rm p}$  and  $N_{\rm NP}$  are the number of matrix polymer chains and nanoparticles in the system). Here NP and tethered monomers are taken as a single rigid body. Since we are interested in the confinement effects on these systems, we have changed the size of the simulation box along X-direction keeping volume fraction of NPs constant. Details of sample systems are given in Table S3. Snapshot of the simulation system is shown in Figure S14.

Table S3: Details of MD simulated systems

System	Number of monomers	Number of monomers	$f = N_{\rm g}/N_{\rm m}$	thicknesses
	in graft chain	in matrix chain	-	
	$N_{ m g}$	$N_{ m m}$		$\sigma$
$\log f$	3	40	0.075	15, 20, 30, 40
high $f$	15	40	0.375	15, 20, 30, 40

All particles are initially placed in a random manner inside the simulation box. A soft cosine potential is applied between the particles to remove the overlap. All quantities are defined in reduced units. All the species of the system interacted through shifted Lennard Jones potential with the following form<sup>12</sup>

$$E = 4\epsilon \left[ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] - E_{\rm rc}$$
(8)

where  $rc = ((D1 + D2)/2)\sigma$  (D1 and D2 are the diameter of the interacting species),  $\epsilon$  is the reduced energy unit and  $E_{\rm rc}$  is the energy cut-off at r = rc.

LAMMPS simulation package is used for MD simulation.<sup>13</sup> The systems were initially equilibrated in NPT ensemble at P = 0 (atmospheric pressure)<sup>14</sup> and in the later stage



Figure S14: a) Snapshot of simulation system (PNC-L): polymer nanocomposite confined between two walls (green and rose in color). This snapshot is generated using Visual Molecular Dynamics (VMD).<sup>11</sup> b) For clarity, matrix polymers from the simulation system is removed. Nanoparticle(orange), tethered monomer (cyan), graft monomer (pink), matrix polymer (brown). Here, graft chain has 3 monomers and matrix chain has 40 monomers.

in NVT ensemble.

Nanoparticle segregation in these systems are studied by plotting density profiles of NPs along the confinement direction as shown in manuscript Fig 2c. NP segregation is estimated using the parameter  $S_{\text{int}}^{\text{sim}}$  defined as the ratio of NPs at the interface to total number of NPs.

#### Viscosity calculation

The viscosity of the systems were calculated using two methods at different temperature regimes. At  $T/T_{\rm g} > 1.55$ , the viscosity is calculated using Green-Kubo relation,.<sup>15</sup>

$$\eta = \frac{V}{k_{\rm B}T} \int_0^\infty \langle \sigma(0)\sigma(t) \rangle \ dt \tag{9}$$

where V is the volume,  $k_{\rm B}$  is the Boltzmann's constant and T is the temperature. At  $T/T_{\rm g} \leq 1.55$ , the viscosity is calculated using the formalism given in the literature.<sup>16</sup>

The viscosity values from both these regimes are merged. Viscosity values obtained using above mentioned methods along with VFT fits are given in Figure S15.

Using VFT equation temperature dependence of viscosity is modeled and slope at  $T = T_{\rm g}$  is calculated as the fragility of the system (Figure S15).



Figure S15: VFT fit of viscosity from simulation a) neat polymer b) low f and c) high f.

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