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Supporting Information

Tuning Mechanical Properties of Nanocomposites with Bimodal Polymer Bound Layers

Erkan Senses and Pinar Akcora

Department of Chemical Engineering and Materials Science

Stevens Institute of Technology, Hoboken, NJ 07030 USA

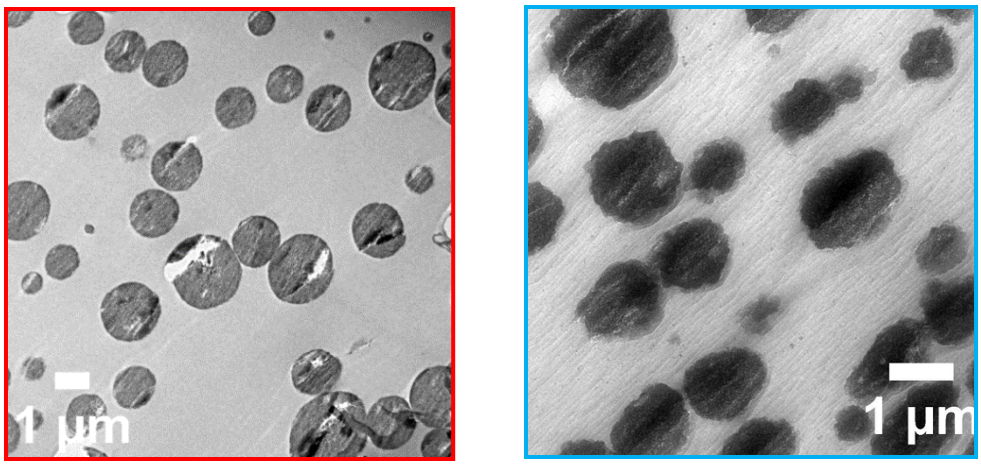

Figure S1. TEM images of 13 nm Silica nanoparticles in PMMA (left image) and PS (right image). Composite films are cast from THF. PMMA matrix consists of 50:50 blends of short (4.3 kg/mol) and long (96 kg/mol) chains. PS matrix consists of 50:50 blends of short (5 kg/mol) and long (100 kg/mol) chains. Particle loadings are 15 wt% in both samples.

Figure S1 shows the effect of solvent on bound layer and dispersion. The choice of solvent influences interaction between polymer and nanoparticles and consequently controls nanoparticle dispersion in polymer nanocomposites. Figure S1 (left image) shows micron-size aggregates of 13-nm Silica particles in PMMA, cast from THF, which is a good solvent for PMMA. THF displaces chains on particle surfaces, preventing formation of a physically bound polymer layer. The observed aggregation reveals the effect of bound layers on particle dispersion. When we changed the polymer to polystyrene, we obtained similar phase separated particles (Figure S1, right image).

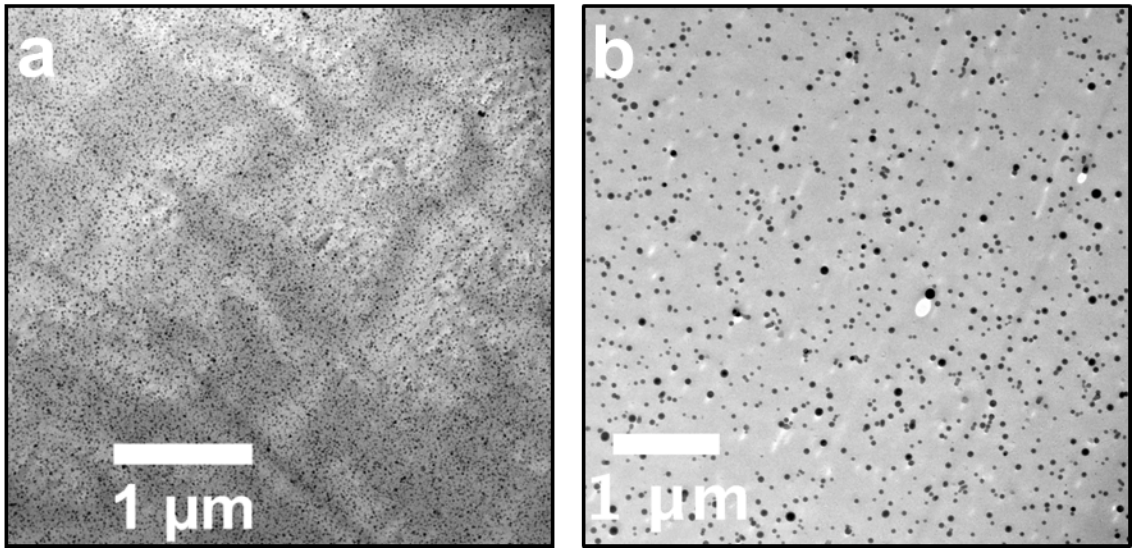

Figure S2. TEM images for (a) 13 nm and (b) 55 nm SiO_2 nanoparticles in 96/4.3 blend PMMA matrix (50/50 vol%). Particle loading is 15 wt% in both samples.

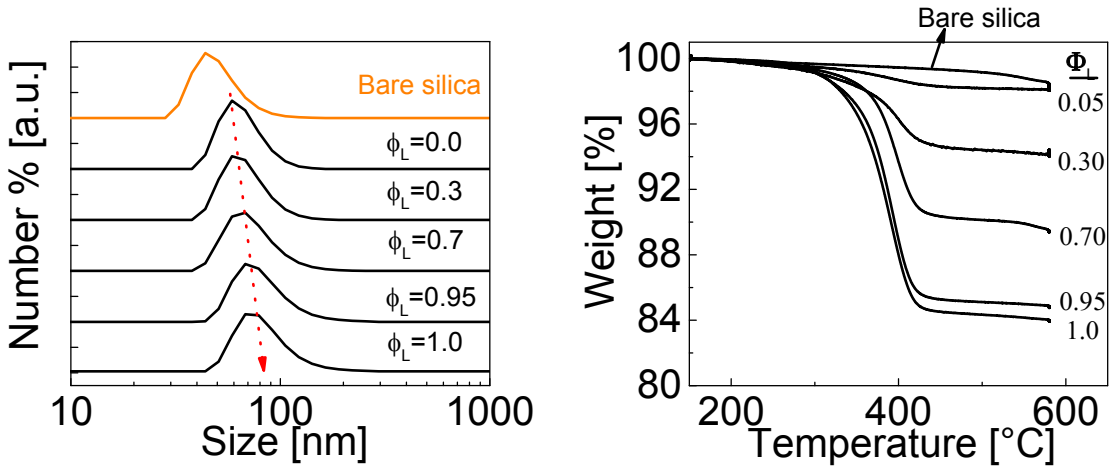

Figure S3. (Left) Hydrodynamic size distributions of 55 nm SiO_2 nanoparticles adsorbed with 68-2.6 kg/mol PMMA blends at varying ϕ_L. (Right) Weight loss curves of corresponding particles are measured in TGA.

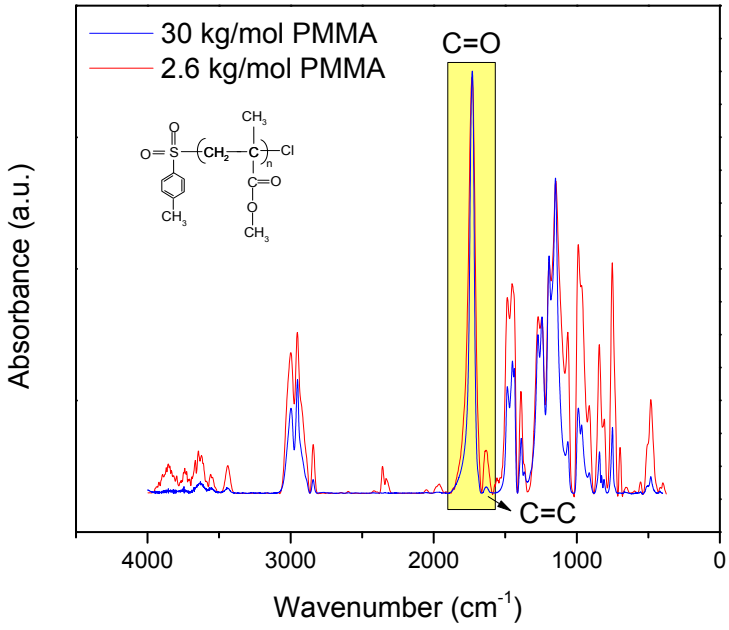

Figure S4. FTIR spectra of PMMA homopolymers at 30 and 2.6 kg/mol.

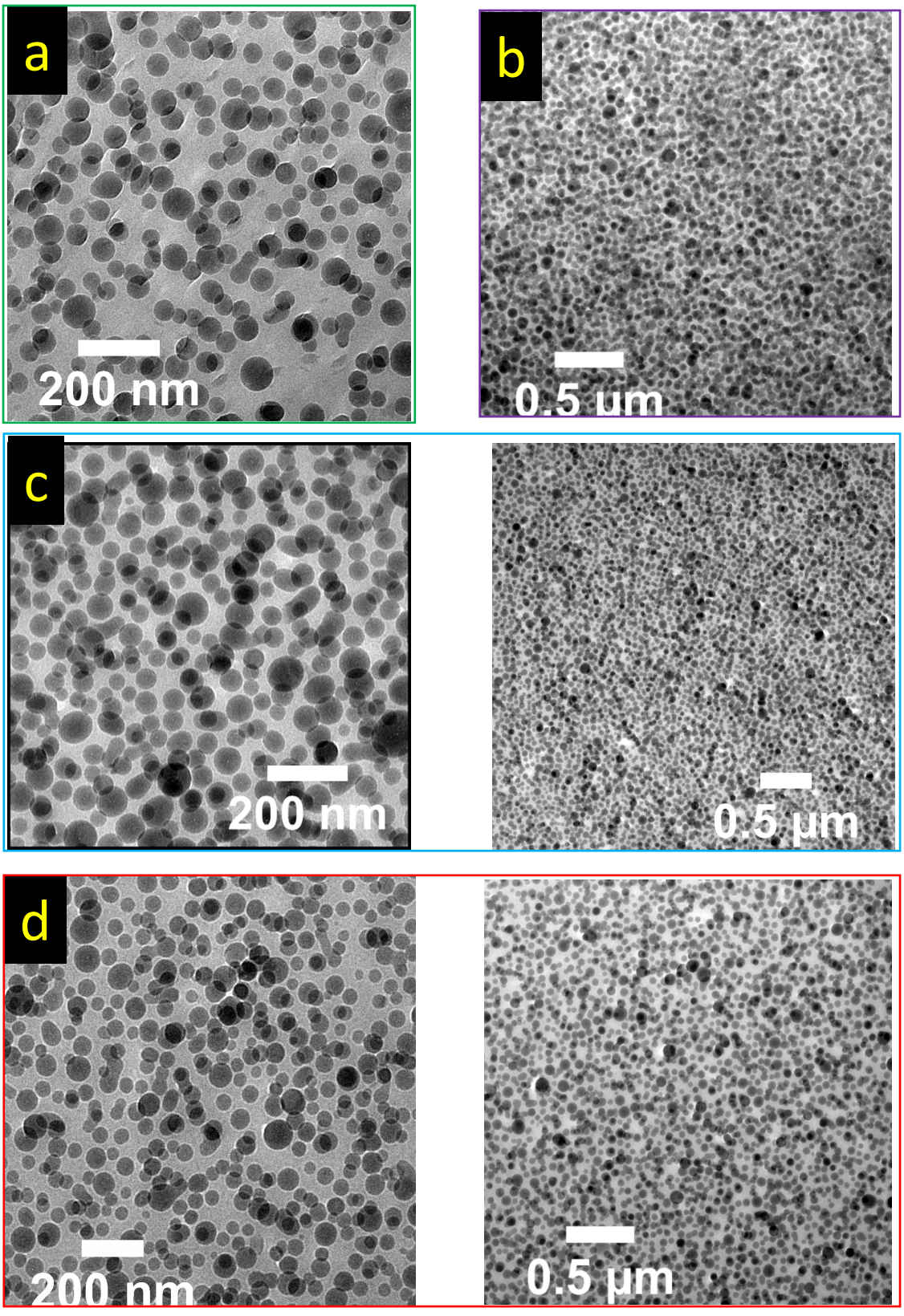
a
200 nm
b
0.5 µm
c
200 nm
0.5 µm
d
200 nm
0.5 µm

Figure S5. TEM images of 55 nm particles adsorbing 68/2.6 kg/mol PMMA blends at varying blend compositions: (a) 50/50 vol%, (b) 100/0 vol%, (c) 70/30 vol%, (d) 30/70 vol% dispersed in 28 kg/mol PMMA matrix. Images next to (c) and (d) are at low magnification. Particle loading is 30 wt% in all composites.

Zero-shear viscosities

We obtained the zero shear viscosities η_0 by fitting complex viscosity data to three-parameter Cross model $\frac{\eta^* - \eta_0}{\eta_0} = \frac{1}{1 + K\omega^m}$. We first obtained parameters for particle-free matrix as $\eta_{0,free} = 5162$ Pa.s, $K_{free} = 0.017$ and $m_{free} = 0.72$. Then, viscosity parameters for the nanocomposite samples were obtained by superposing the contributions of free and interphase. We kept the matrix contribution the same as the particle loading is constant, and only allow the interphase parameters to change in the composite viscosity to give $\eta^* = \eta^*_{free} + \eta^*_{interphase}$. Because polymer is the same in the interphase, we kept the exponent the same for free chains $m_{free} = m_{interphase} = 0.72$. We then obtained the parameters $K_{interphase}$ and $\eta_{0,interphase}$ for each bound layer composition ϕ_L. Contributions from free and interphase polymer and their superposition is illustrated on the composite with ϕ_L = 1 in Figure S6. Fittings for all composites are shown in Figure S7. Fitting parameters for the interphase contributions in each sample are given in Table S1. The overall zero shear viscosity then becomes $\eta_0 = \eta_{0,free} + \eta_{0,interphase}$.

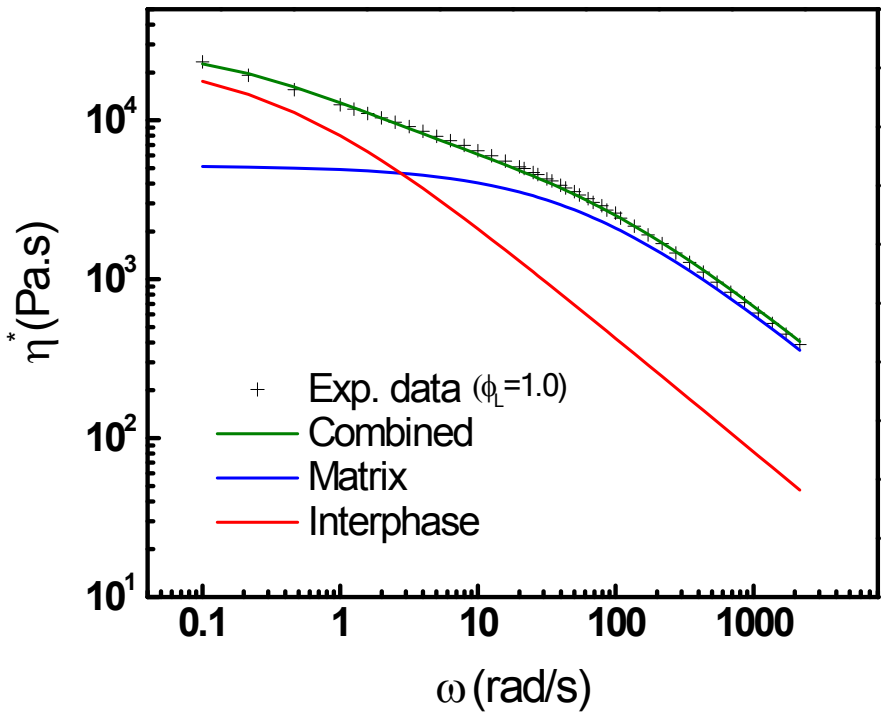

Figure S6. Complex viscosity response of composite with ϕ_L = 1 obtained from linear viscoelastic results shown in Figure 4 and corresponding model fit. Solid lines are free and interphase polymer contributions to the composite viscosity.

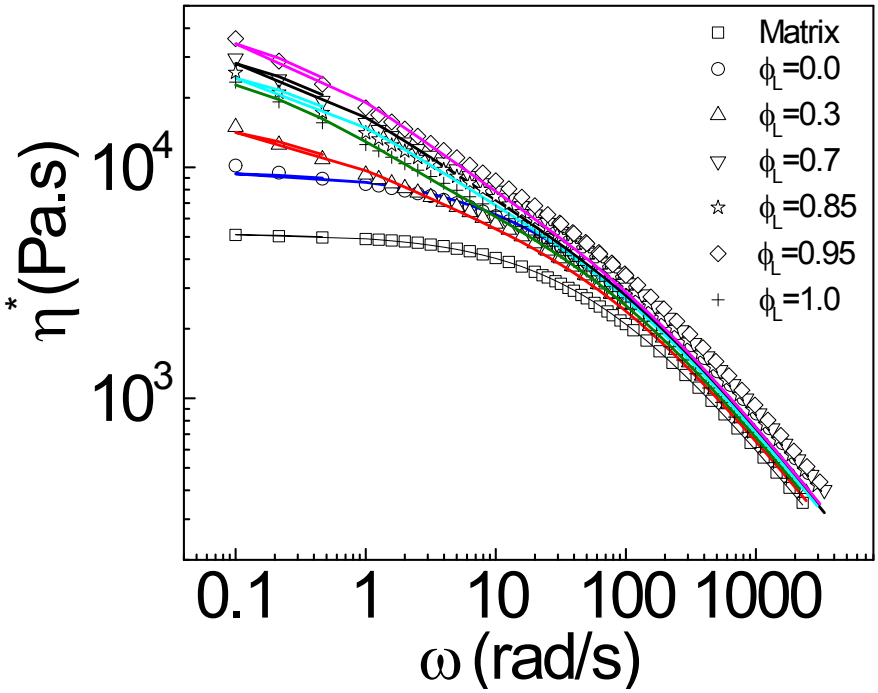

Figure S7. Model fittings for all composites and matrix homopolymer presented in Figure 4.

Table S1. Fitting parameters for interphase contribution to the complex viscosity.

	Interphase		
ϕ_L	η_0	K	m
1	24489.91	2.72921	0.72
0.95	38762.75	2.15014	0.72
0.85	24625.23	1.7276	0.72
0.7	30103.35	1.94921	0.72
0.3	11480.2	1.60544	0.72
0	4417.614	0.10134	0.72

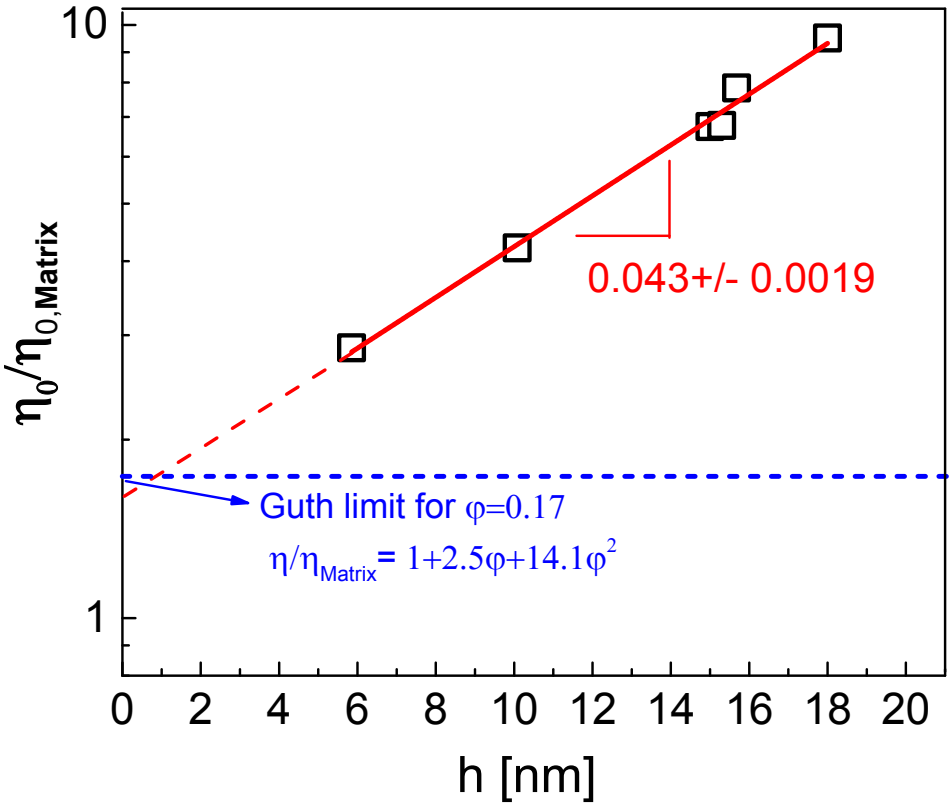

Figure S8. Relative zero-shear viscosities as a function of hydrodynamic size (h) of particles. Flat line is the Guth prediction for spherical particles at high loadings. Particle loading is 30 wt%.

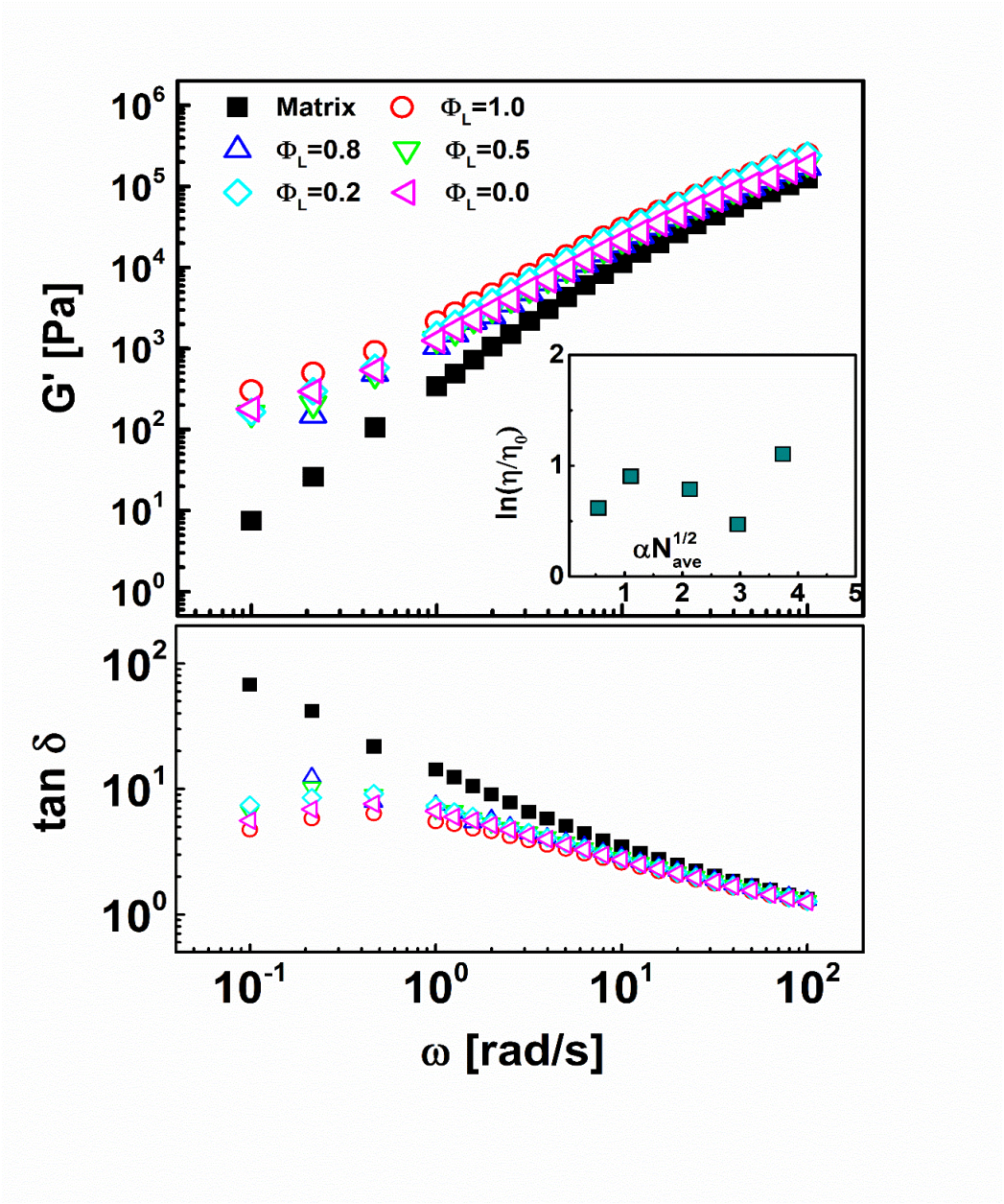

Figure S9. Linear elastic modulus and loss tangent of nanocomposites with 12/2.6 kg/mol PMMA blend adsorbed on SiO_2 (55 nm) nanoparticles dispersed in 28 kg/mol PMMA (T = 210 ^{o}C). Inset shows reinforcement factor calculated from zero shear viscosity. Particle loading is 30 wt%.

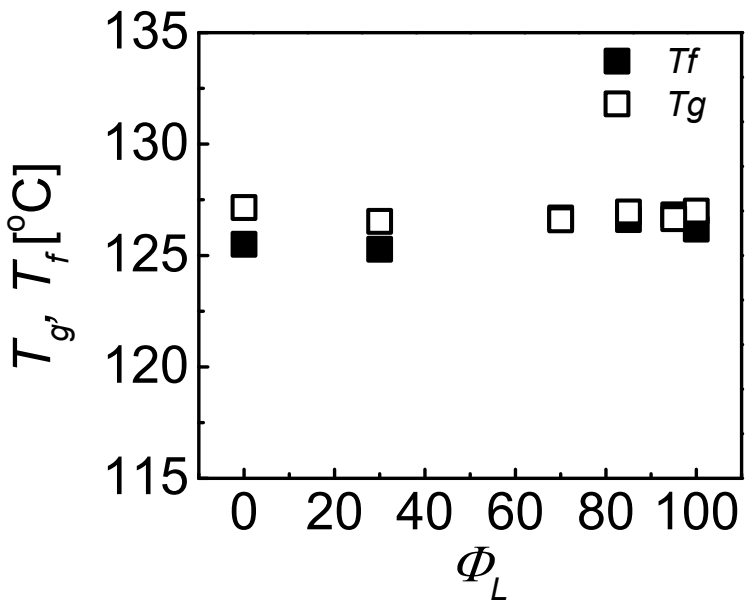

Figure S10. Glass transition (T_g) and fictive (T_f) temperatures of nanocomposites with varying long chain fraction in bound layer.