Kumar SK, Benicewicz BC, Vaia RA, Winey KI 50th Anniversary Perspective: Are Polymer Nanocompsites Practical for Applications? Macromolecules **50** 714-731 (2017).



Figure 1. Schematic illustration of the various types of NP available, the forms of surface functionalization, and the applications that these materials can impact.

So, take an example You are interested in **flame retardancy** and have two routes:

Pick a polymer with inherent flame retardancy like Teflon[®] (thermally stable, low flame propagation) or polyimides (large char) or polysiloxanes (inorganic components to polymer)

Add a material with high thermal conductivity, high heat capacity, char formation or protection of

char that is formed (and is cheap) like Exfoliated clay works. Silica, titania. Calcium carbonate

polyimide



polybenzimidazole





Flame Retardant Polymer

Nanocomposites: An Overview Kumar S(different one), Dhawan R, Shukla SK Macromol. Symp. 407 2200089 (2023).

polybenzoxazole



polybenzthiazole



Table 2. Comparison between the preparation methods of polymer nanocomposites.

S. No.	Methods		Advantages	Disadvantages	Ref.
1.	Ex-situ method	Solution casting	High production,	Solvent required, more impurity	[21]
		Melt compounding	The more pure final product, high production	High viscosity, cleaning problem	[21]
2.	In situ method	Chemical synthesis	Micro indentation, easy control	Costly and time-consuming	[22]
		Photochemical synthesis	Better compatibility, pure products.	Higher reactivity, costly, control environment required.	[23]
		Electrochemical synthesis	Synthesized in a moderate environment, i.e., at normal room temperature and pressure.	Reactions are restricted to the working electrodes' surfaces.	[24]



Figure 2. Design and synthesis of CuP-MXene. a) Schematic illustration for the preparation process of CuP-MXene; b) TEM image of MXene; c) TEM image of CuP-MXene; d) SEM image of CuP-MXene.

Flame Retardant Polymer Nanocomposites: An Overview Kumar S(different one), Dhawan R, Shukla SK Macromol. Symp. **407** 2200089 (2023).

The original nanocomposite

Polydisperse aggregates

Processed under shear

Kinetically mixed



Objective: Tear resistance Static charge dissipation



100,000 x larger

Song, L; Wang, Z; Tang, X.; Chen, L.; Chen, P.; Yuan, Q.; **Li, L.** Visualizing the Toughening Mechanism of Nanofiller with 3D X-ray Nano-CT: Stress-Induced Phase Separation of Silica Nanofiller and Silicone Polymer Double Networks Macromolecules 50 7249-7257 (2017).



Kumar, S.K., Jouault, N., Benicewicz, B. and Neely, T., 2013. Nanocomposites with polymer grafted nanoparticles. *Macromolecules*, 46(9), pp.3199-3214.

Kumar, S.K., Benicewicz, B.C., Vaia, R.A. and Winey, K.I., 2017. 50th anniversary perspective: are polymer nanocomposites practical for applications?. *Macromolecules*, *50*(3), pp.714-731.

Asai, M., Zhao, D. and Kumar, S.K., 2017. Role of grafting mechanism on the polymer coverage and self-assembly of hairy nanoparticles. ACS Nano, 11(7), pp.7028-7035.

The original nanocomposite

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L. Pahalagedara, H. Sharma, C.H. Kuo, S. Dharmarathna, A. Joshi, S.L. Suib, A.B. Mhadeshwar, Structure and oxidation activity correlations for carbon blacks and diesel soot, Energy and Fuels. 26 (2012) 6757–6764

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Mulderig, A., Beaucage, G., Vogtt, K., Jiang, H. and Kuppa, V., 2017. Quantification of branching in fumed silica. *Journal of Aerosol Science*, *109*, pp.28-37. Beaucage, G. Approximations Leading to a Unified Exponential/Power-Law Approach to Small-Angle Scattering. J. Appl. Crystallogr. 1995, 28, 717–728.

7

Multiscale Hierarchical Structures (Dilute)



в

200 nm

393 kDa polystyrene

75 kDa polystyrene

q (Å⁻¹)

С



Fig. 2. (**A**) Cartoon showing branched, dendritic polyethylene. (**B**) TEM of a 4 wt % blend of dendritic polyethylene with 393-kD linear polystyrene shows the individual polyethylene macromolecules with a size on the order of 20 to 30 nm. The R_g for the linear polystyrene is 17.4 nm and so is larger than the dendritic polyethylene. (Inset) A higher magnification. (**C**) Mixing with a smaller molecular mass polystyrene (75 kD, $R_g =$ 7.5 nm) produces phase separation. Power law scattering of intensity (*I*) versus wave vector (*q*) is present at small wave vector for the lower mass polystyrene, whereas the higher mass system demonstrates miscibility without a power law region. The intensity profile can be fitted with a

polydisperse sphere model, yielding a mean radius (11.0 nm) for the dendritic polyethylene that agrees well with the TEM images.

10³

10²

10¹

10⁰ 🔽

10⁻¹

Power law 3.85 ± 0.02

6 7 8 9 10⁻²

l(q) (cm⁻¹)

Studied C60 (Buckeyballs) in PS; PS NP in PS; and dendritic PE in PS

When chains are larger than particles system is "dispersed"

Linear chains are swelled in the presence of nanoparticles, R_g grows with volume fraction NP



9

An enthalpic mechanism that arises from nanoparticle packing effects operates at the nanoscale and is necessary in order to understand dispersion in this size regime.

-Polymer blend "Chain insertion enthalpy" = $N\chi$ -"NP insertion enthalpy" = $A\chi = 4\pi a^2\chi$

-Dispersion depends on processing

-When
$$\phi_p \sim 0$$
 the binodal is defined by
 $\phi_p \sim \exp(-(1 + N\chi))$
for NP $\phi_p \sim \exp(-(1 + 4\pi a^2\chi))$
The limit of dispersion of C60 is 2%
so, $\chi \sim z\varepsilon/kT$ and $\varepsilon \sim 0.02$ eV
Can quench a super-saturated "solution"



Fig. 1. (**A**) Rapid precipitation of fullerenepolystyrene blends, followed by drying and melt processing, allows manufacture of fibers. The fibers contains 1 wt % C_{60} fullerenes that were melt spun into long fibers with a diameter of circa 1 mm. (**B**) Fullerene (1 wt %)-polystyrene blends developed through regular solvent evaporation produce large, phase-separated domains, which are not apparent in the fiber.

1.17

relative to that without nanoparticle incorporation (R_g/R_{g0}) is expected to vary as $(1 + \phi)^{\frac{1}{3}}$. The chain stretching is larger than the amount suggested by this relationship and is empirically close to $1 + c\phi$, with *c* about 1. When chains are larger than particles system is "dispersed"

Linear chains are expanded when in the presence of nanoparticles

Excluded volume $(1 + \phi)$ predicts $(1 + \phi)^{1/3}$



relative to that without nanoparticle incorporation (R_g/R_{g0}) is expected to vary as $(1 + \phi)^{\frac{1}{3}}$. The chain stretching is larger than the amount suggested by this relationship and is empirically close to $1 + c\phi$, with *c* about 1.

Fig. 3. (A) The polymer radius of gyration (R_{n}) relative to that without nanoparticles (R_{ao}) for three different molecular mass linear polystyrenes: 21, 63, and 155 kD, as a function of volume fraction (o) of 52.0-kD tightly cross-linked polystyrene nanoparticles. The nanoparticles stretch the polymer chains. The solid line represents the radius of gyration variation if the polymer density does not change upon mixing, and the behavior $(1 + \phi)^{1/3}$ is expected. Instead, the data obeyed $1 + c\phi$, with c about 1. The error bars represent the error from a Guinier fit to the data at small wave vector. (B) A polymer radius of gyration-nanoparticle radius phase diagram, with the solid circles representing data where phase separation was detected and the open circles where miscibility occurs. Open circles



with an \times represent conditions where some agglomeration was detected by SANS yet large-scale phase separation was not observed. Squares are the C₆₀ polystyrene system; circles, the polystyrene nanoparticle–polystyrene system; and triangles, the dendritic polyethylene–polystyrene system. The dashed line represents the reptation tube radius, suggesting phase stability does not depend on the entanglement structure. The nanoparticle fraction used to generate each data point was 2 wt %. (**C**) Cartoon illustrating that the attraction between pure nanoparticles is effective only over a fraction (A_c) of the available surface area (A) because of the limited range (δ) over which dispersion forces operate.

When chains are larger than particles system is "dispersed"

For PS NP in dPS a negative χ is found (compared to positive for PS in dPS)

Short-range VdW forces between particles only act in the orange region. Polymer/NP interaction acts over the whole surface. So, dispersion is favored. The VdW area (orange) changes with particle size.

The mixing enthalpy of a nanoparticle, s, can be related to the Flory parameter via $s = A_C \chi + A_U (\chi - \varepsilon_{np}/k_B T) \equiv s_0 - s_1$. Here $s_0 = A\chi$ is the insertion enthalpy in the absence of geometric effects due to uncovered area, and $s_1 = A_U \times \varepsilon_{np}/k_B T$ is the reduction in enthalpy within the pure nanoparticle phase due to uncovered area.



 $(A_{\rm C}) = (z\delta/4a) \times A$

(**B**) A

polymer radius of gyration—nanoparticle radius phase diagram, with the solid circles representing data where phase separation was detected and the open circles where miscibility occurs. Open circles

with an \times represent conditions where some agglomeration was detected by SANS yet large-scale phase separation was not observed. Squares are the C₆₀-polystyrene system; circles, the polystyrene nanoparticle-polystyrene system; and triangles, the dendritic polyethylene-polystyrene system. The dashed line represents the reptation tube radius, suggesting phase stability does not depend on the entanglement structure. The nanoparticle fraction used to generate each data point was 2 wt %.

Schadler LS, Kumar SK, Benicewicz BC, Lewis SL, Harton SE Designed Interfaces in Polymer Nanocomposites: A Fundamental Viewpoint MRS Bulltin **32** 335-340 (2007).

Why nanoparticles?

First, they can have properties distinct from micron-scale fillers. For example, carbon nanotubes are as stiff as graphite fibers, but are almost an order of magnitude stronger.

Second, nanoscale fillers play the role of small mechanical, optical, and electrical defects. These provide an opportunity for multi- functionality (e.g., scratchresistant, transparent polymers).

Third, they create a large volume of interfacial polymer with properties different from the bulk, providing an opportunity for tailoring properties.



Figure 1. (a), (b) Schematic illustrations showing the difference in the volume of interfacial polymer (shown in blue) for nanocomposites compared with micron-scale composites. The area of red is about the same in the two images. (c) Schematic illustrations showing that the properties of the polymer change as a function of distance from the particle surface. (d) Scanning electron micrograph of a nanotube/polycarbonate fracture surface, showing the interface zone on the nanotube.¹⁰



Figure 2. Comparison between the glass-transition response of polystyrene nanocomposites and polystyrene thin films as a function of interparticle spacing, which represents the film thickness for thin films and an average interparticle spacing in the nanocomposites. The x-error bars represent a 95% confidence level. Data from literature on freestanding ultrathin films²⁹ and supported films³⁰ are shown as open circles. (Taken from Reference 31.)



Figure 3. Plot showing the effect of the difference in the solubility parameters multiplied by the surface area as a function of glass-transition temperature. The glass-transition data include melt-processed ZnO/polystyrene⁵⁰ and calcium carbonate/poly(methyl methacrylate) composites⁵¹ with several surface modifications as well as data generated by our group on solution-processed silica/polystyrene nancomposites using both as-received and fluorinated 15-nm silica.⁶⁴



Figure 4. Plot of the effective interaction parameter, χ_{eff} , for a matrix of effectively infinite molecular weight as a function of graft chain length. The three plots correspond to three different grafting densities, (a) $\sigma = 0.50$, (b) $\sigma = 0.66$, and (c) $\sigma = 0.77$, where in each plot the three lines correspond to three different particle diameters. These diameters are in units of lattice units, where each site is ~1 nm. The dashed lines show that $\chi_{\text{eff}} \sim N_{\text{G}}^{-1.1,57}$

An effective mean-field interaction (χ_{eff}) that arises because of the entropic penalty associated with the interface formed between the brush and the matrix chains.

Lower χ means greater "miscibility"

Matrix is infinite molecular weight

Top low graft density, σ , bottom high

Larger particles have lower "miscibility" Three curves

Greater miscibility with longer graft chain length



Figure 5. Plots of (a) the change in glass-transition temperature (ΔT_g) as a function of SiO₂ concentration for silica nanoparticles with 110,000 g/mol polystyrene on the surface, graft density of 0.27 chains per nm², and matrix of various molecular weights (in g/mol), shown at the right in the Figure. Dashed lines are a guide for the eye.⁶³ (b) The change in glass-transition temperature T_g for polystyrene-grafted silica/ polystyrene nanocomposites as a function of the graft density σ , multiplied by the chain length of the grafted chain $N_{\rm G}$.⁶⁴

Vary matrix MW for 110,000 g/mole grafts of PS on silica in PS

Vary matrix MW for 110,000 g/mole grafts of PS on silica in PS



Figure 5. Plots of (a) the change in

Chatterjee T, Jackson A, Krishnamoorti R *Hierarchical Structure of Carbon Nanotube Networks* JACS **130** 6934-6935 (2008).



Figure 1. (a) Concentration effect corrected scattering data lead to a master curve indicating a hierarchical network structure over a wide length scale range. (b) A schematic of the hierarchical network structure showing different length scales; we note that the mesh size and floc sizes could be quite polydisperse.



Figure 3. Concentration dependence of the network mesh size (ζ) and the Guinier prefactor of the highest structural level (G_1) in different matrices. The scaling of ζ is consistent with diffusion-limited cluster formation, while the dependence of G_1 suggests that the number of flocs grows linearly with the concentration of nanotubes. The error bars shown here and in the rest of the paper correspond to ± 1 standard deviation, obtained from the fitting of the scattering data to the model.



p/p _c	fractal dimension (d)	floc size (µm)
Bisphenol F		
1.2	2.9 ± 0.1	4.3 ± 0.2
2.0	2.9 ± 0.1	4.4 ± 0.2
4.0	2.9 ± 0.1	3.6 ± 0.1
Bisphenol A		
1.5	3.0 ± 0.1	4.1 ± 0.2
2.5	2.9 ± 0.1	4.4 ± 0.3
5.0	2.9 ± 0.1	4.9 ± 0.1
PEO		
4	2.4 ± 0.1	3.9 ± 0.4
6	2.3 ± 0.3	3.2 ± 0.2
7	2.3 ± 0.2	3.5 ± 0.2
8	2.2 ± 0.3	3.8 ± 0.4
10	2.3 ± 0.1	3.3 ± 0.3
15	2.2 ± 0.2	3.6 ± 0.2



Quantitative measure of nano-dispersion (Mean Field)

- The rate of decrease in $I(q)/\phi$ with concentration in this intermediate q-range is an indicator of how well the filler is dispersed in the elastomer. v
- This diminution is directly related to the molar excluded volume per aggregate, B_2 .



Interaction leads to structural screening

Pedersen, J. S.; Sommer, C. Temperature Dependence of the Virial Coefficients and the Chi Parameter in Semi-Dilute Solutions of PEG. In *Scattering Methods and the Properties of Polymer Materials*; Springer Berlin Heidelberg; Berlin, Heidelberg; 2005; pp 70–78.

Vogtt, K.; Beaucage, G.; Weaver, M.; Jiang, H. Thermodynamic Stability of Worm-like Micelle Solutions. Soft Matter 2017, 13 (36), 6068-6078.

Jin, Y.; Beaucage, G.; Vogtt, K.; Jiang, H.; Kuppa, V.; Kim, J.; Ilavsky, J.; Rackaitis, M.; Mulderig, A.; Rishi, K.; Narayanan, V. A Pseudo-Thermodynamic Description of Dispersion for Nanocomposites. *Polymer (Guildf)*. 2017, *129*, 32–43.

Greg Beaucage, University of Cincinnati gbeaucage@gmail.com

(174) Jouault, N.; Moll, J. F.; Meng, D.; Windsor, K.; Ramcharan, S.; Kearney, C.; Kumar, S. K. Bound Polymer Layer in Nanocomposites. ACS Macro Lett. 2013, 2, 371–74.



Figure 3. Schematic illustration of the presence of a bound layer and a layer of intermediate mobility in a filled elastomer. From ref 174.

ABSTRACT: There has been considerable interest in characterizing the polymer layer that is effectively irreversibly bound to nanoparticles (NPs) because it is thought to underpin the unusual thermomechanical properties of polymer nanocomposites (PNC). We study PNCs formed by mixing silica nanoparticles (NPs) with poly-2-vinylpyridine (P2VP) and compare the bound layer thickness δ determined by three different methods. We show that the thickness obtained by thermogravimetric analysis (TGA) and assuming that the bound layer has a density corresponding to a dense melt clearly underestimates the real bound layer thickness. A more realistic extent of the bound layer is obtained by in situ



measurements of the interaction pair potential between NPs in PNCs via analysis of TEM micrographs; we verify these estimates using Dynamic Light Scattering (DLS) in θ solvent. Our results confirm the existence of long-ranged interactions between NPs corresponding roughly in size to the radius of gyration of the bound chains.

Yi C, Zhang S, Webb KT, Nie Z Anisotropic Self-Assembly of Hairy Inorganic Nanoparticles Accounts of Chem. Res. **50** 12-21 (2017).

As σ exceeds the overlap threshold of chains, polymers are stretched from anchor points toward the solvent medium, entering the semidilute polymer brush (SDPB) regime. At even higher σ , the concentrated polymer brush (CPB) regime is accessed, which is featured by non-Gaussian chain characteristics and more extended chain conformations.



Figure 1. Schematic illustration of three regimes of polymeric brush conformation on NP surfaces. Reprinted with permission from ref 5. Copyright 2013 Material Research Society.



(132) Rungta, A.; Natarajan, B.; Neely, T.; Dukes, D.; Schadler, L. S.; Benicewicz, B. C. Grafting Bimodal Polymer Brushes on Nanoparticles Using Controlled Radical Polymerization. Macromolecules 2012, 45, 9303–11.

Thermally dispersed particles

Diffusion is more efficient for smaller particles

Greater grafting density improves colloidal dispersion

Figure 2. Map of the grafting density vs the ratio of the NP size and chain radius of gyration. A = amorphous aggregates, H = sheets, C = chains, and D = dispersed NPs. Adapted from ref 132.

Akcora P, Liu H, Kumar SK, Moll J, Li Y, Benicewicz BC, Schadler LS, Acehan D, Panagiotopoulos AZ, Pryamitsyn V, Ganesan V, Ilavsky J, Thiyagarajan P, Colby RH, Douglas JF *Anisotropic self-assembly of spherical polymer-grafted nanoparticles* Nat. Mat. **8** 354-359 (2009).



Model:

Short-range attraction $\delta \varepsilon/kT$ fitting parameter (attraction) Countered by entropy of distortion of grafted polymer chains Entropy of distortion from coilglobule transition model

Figure 1 | Theoretical predictions and comparison of theory to experiments. a, Simulation snapshots for particles with six uniformly spaced grafts, going from bare particles forming spherical aggregates, to flattened cylinders with N = 2; branched cylinders with thinner arms N = 5; sheets with N = 6 (sheet shown in the detail); long strings with N = 8 (only one string shown); short chains with N = 10 (not shown); and isolated particles with N = 14. The stable state of the ungrafted particles under these conditions should be a crystal. Thus, the liquid droplet seen here is a metastable state. **b**, Results of simulations and theory at different grafting densities. Polytetrahedra, that is, sheets with a tetragonal packing of particles, and sheets with a two-dimensional hexagonal packing of particles are both designated as 'sheets'. Lines are predictions of analytical theory; symbols are from simulation. Red symbols: spheres, dark blue: sheets, light blue: strings, magenta: well-dispersed particles. **c**, Experimental 'morphology diagram' of polymer-tethered particles mixed with matrix polymers. Red symbols are spherical aggregates, blue symbols are sheets and interconnected structures, cyan symbols are short strings and purple symbols are dispersed particles. The lines that separate the different regions are merely guides to the eye.



Figure 2 | Experimental study of particle self-assembly. a, TEM-determined temporal evolution of particle structuring. In all cases, 5 mass% silica grafted with a $M_g = 106 \text{ kg mol}^{-1}$ polystyrene brush with 37 chains per particle (0.05 chains nm⁻²) is mixed with polystyrene matrices of different *M*: 17, 42, 142 and 272 kg mol⁻¹, respectively, and annealed at 150 °C for a range of times as noted in the figure. Sheet formation was observed in the composite with matrix $M = 142 \text{ kg mol}^{-1}$ sample after 3 days of annealing and in the matrix $M = 272 \text{ kg mol}^{-1}$ after 19 days. The scale bar in all cases is 0.5 µm, and the sections were cut normal to the film surface. **b.c**, Effect of variations in grafting density and molecular weight of tethered chains (M_g) on particle dispersion and self-assembled structures after annealing for 5 days at 150 °C. Increased brush molecular mass (M_g) and increasing grafting density have similar effects on the aggregation process: with increasing graft polymer coverage, we thus progressively go from spherical clusters, to thick sheets, thin sheets, strings and finally well-dispersed particles. The thick to thin sheet transition is continuous and hence we classify them both as sheets. The matrix homopolymer is 142 kg mol⁻¹ in **b** and 42 kg mol⁻¹ in **c. d**, USAXS data (symbols) and unified fits (solid lines) of samples shown in the first row and in the second row of **b**, respectively. The fit parameters are reported in Supplementary Table S3.



The TEM data in Fig. 2a were taken from slices normal to the surfaces. We have taken 15 adjacent ≈ 100 -nm-thick slices from a film with a matrix of M = 142kgmol⁻¹, which show string-like morphologies in Fig. 2a, and find that the same 'string- like' structure is seen in each slice (see Supplementary Fig. S4b). Consequently, these objects are sheet-like. We have also analysed slices parallel to the casting surface and found qualitatively similar results (see Supplementary Fig. S4c). Evidently, these particles spontaneously assemble into sheets that are 2–5 particles (<100 nm) wide with lateral dimensions in the 1–10 µm range. A point to note here is that we see only hexagonal particle packings in the sheets (see Supplementary Fig. S5d). We do not see the other packings predicted by the theory/simulation.

Akcora P, Liu H, Kumar SK, Moll J, Li Y, Benicewicz BC, Schadler LS, Acehan D, Panagiotopoulos AZ, Pryamitsyn V, Ganesan V, Ilavsky J, Thiyagarajan P, Colby RH, Douglas JF *Anisotropic self-assembly of spherical polymer-grafted nanoparticles* Nat. Mat. **8** 354-359 (2009).

Supplementary Table 3. Primary particle and cluster sizes obtained from Beaucage unified fits to the USAXS data at different q regions for data shown in Fig. 2d.

² Brush M _g	High q-Primary	Low q-Cluster	Intermediate q	Low q-Power]
(kg/mol)	particle R _g (Å)	R _g (Å)	R _g (Å)	law	4
			These are o	it and the second	÷.
25	45	869	correlated	or s&peen	ed
Fractal d _f ~	1 (53)	847	Fractal o	faggøega	tes
158	56	6034	499 d	_f ~ <u>1</u> ^{3.1}	
17	150	7150		3.6	1
34	139	Fractal d.	~ 1	3.5	
106	227	i lactal u _f	1	3.6	

The USAXS gives the size of the primary particles, and also indicates the existence of larger scale mass fractal structures (with fractal dimension ~ 3). It is unclear why the particle sizes vary in the last three rows, while they remain relatively constant for the first three rows. We conjecture that this might represent local particle clustering. USAXS does not provide the dimensions of the large-scale clusters seen in the second row of Fig. 2b (samples with brush molecular mass of 34 and 106 kg/mol. respectively). This indicates that the cluster sizes are larger than 1 μ m.



Supplementary Figure 2. Comparison of the storage (G') and loss (G") modulus of the PS composites containing 0 and 5 mass% silica particles in a matrix M=42 kg/mol (black) and M=142 kg/mol (red) as a function of the shifted frequency. Filled symbols refer to nanocomposites and open symbols are for matrix homopolymers. Master profile is obtained by time-temperature superposition at the reference temperature T=180°C.



Circle G"; Square G'

Filled = 5% Nanocomposite Open = Polymer

Red = 142 kg/mole (Large Sheets) Black = 42 kg/mole (Short Strings)

180°C

We select two samples corresponding to the images in Fig. 2a in the main text where the particles are grafted with 37 chains of M_g = 106 kg/mol: one with well dispersed short particle strings (matrix M= 42 kg/mol) and the other where there are large self-assembled particle sheets (matrix M=142 kg/mol). The linear rheology of these nanocomposites (Supplementary Fig. 2) shows that the lower molecular weight matrix nanocomposite is analogous to a blend of linear and star polymers.⁵ The relaxation at tens of rad/s is that of the linear homopolymer matrix and the relaxation at tenths of rad/s is that of (essentially) isolated spherical

nanobrushes, analogous to a slower relaxing star polymer. Thus, the storage modulus for example decreases strongly with decreasing frequency. The larger molecular weight matrix in stark contrast does not relax in the frequency range studied, instead exhibiting a much slower dependence on frequency. These results, which suggest that this latter sample behaves akin to a reversible gel, cannot be attributed to changes in polymer glass transition temperature due to the addition of particles: the T_g changes by less than 3K in all nanocomposites that we have measured.



Figure 3 | Shear-stress response to steady-shear application at 180 °C at a shear rate of 0.1 s⁻¹ for composites with matrix M = 42 kg mol⁻¹ (black) and 142 kg mol⁻¹ (red) and of pure homopolymers. Each particle, on average, has 37 chains grafted to it, where each grafted chain was of molecular mass of 106 kg mol⁻¹. The blue symbols are for a matrix with 142 kg mol⁻¹ but for particles that have six chains grafted to them, with each of them of 158 kg mol⁻¹. The left axis is for the M = 142 kg mol⁻¹ and the right axis is for the 42 kg mol⁻¹ matrix. The open symbols are for the homopolymer and the filled symbols are for the nanocomposite. Kumar SK, Jouault N, Benicewicz B, Neely T *Nanocomposites with Polymer Grafted Nanoparticles* Macromolecules **46** 3199-3214 (2013).



Figure 1. Broad area covered by review. Discussion is primarily on the left side of this diagram, in the case of "homopolymer" brushes.

Scheme 1. Synthesis of Bimodal Brush Particles Using Sequential RAFT Polymerization





Figure 3. Grafted chain thickness δ in (a) PNCs and in (b) solvent as determined by small-angle neutron scattering (SANS). Using an appropriate contrast variation, one can match the silica scattering to the matrix polymer and thus only measure the signal of the grafted corona. The continuous lines are the best fits using a Gaussian chain model (a) and a "core/shell" model (b). Adapted from ref 147.



 $1/\alpha$ = Matrix/Graft MW 0.1 short matrix MW 10 long matrix MW

Figure 4. A composite morphology diagram created from all of the available data in the literature: $\sigma \sqrt{N}$ as a function of $1/\alpha$ with $\alpha = N/P$. The points, adapted from the literature, are color coded so that a red point corresponds to well dispersed particles (WD); black to phase separated samples (PS); blue to strings (S); green to connected sheets (CS) and purple to small clusters (SC). The color-coded lines represent a first-order cut at classifying the data into well defined regions in the plot where different morphologies occur. This classification is not perfect – for example, there are black squares in a red region. (\Box) is for 18 nm PS-g-SiO₂ NP from ref 29, (\times) for 10 nm PEO-g-SiO₂ NP from ref 44, (\blacklozenge) for 17 nm PS-g-SiO₂ NP from ref 160, (\bigcirc) for 14 nm PS-g-SiO₂ NP from ref 46, (\triangle) for 28 nm PS-g-SiO₂ NP from ref 154, (—) for 12 nm PBA-g-SiO₂ NP from ref 207, and (+) for 8 nm PS-g- γ -Fe₂O₃ NP from ref 220.

Kumar, S.K., Jouault, N., Benicewicz, B. and Neely, T., 2013. Nanocomposites with polymer grafted nanoparticles. *Macromolecules*, *46*(9), pp.3199-3214.



Akcora P, Liu H, Kumar SK, Moll J, Li Y, Benicewicz BC, Schadler LS, Acehan D, Panagiotopoulos AZ, Pryamitsyn V, Ganesan V, Ilavsky J, Thiyagarajan P, Colby RH, Douglas JF *Anisotropic self-assembly of spherical polymergrafted nanoparticles* Nat. Mat. **8** 354-359 (2009).

Figure 5. TEM determined temporal structuring. In all cases 5 mass % silica grafted with a variety of graft molecular weights, M_g , of a polystyrene brush with varying grafting densities, σ , is mixed with polystyrene matrices of M = 142 kg/mol and annealed at 150 °C for 5 days. The scale bars are 0.5 μ m. Adapted from reference 46.



Figure 6. Time evolution of the bulk structures formed by 14 nm diameter silica NP grafted with PS chains (106K, 0.05 chains/nm²) in a PS matrix (231K): (a) as cast, (b) annealed for 3 days, and (c) annealed for 5 days at 150 °C. The samples were annealed for up to 28 days, and the structures continue to grow.



Figure 7. Mean-square displacement $\langle u^2 \rangle$ obtained by QENS for welldispersed (black symbol) and aggregated (red symbol) NP states. Reproduced from ref 184.



Figure 8. TEM micrograph of 14 nm silica nanoparticles grafted with a 80K poly(n-butyl acrylate). The sample was drop-cast on a TEM grid and then imaged. Adapted from ref 155.



Figure 9. (A) TEM images showing nanoparticle dispersion states. All three samples have a 142 kg/mol matrix. Left: agglomerated, 25 kg/mol graft, 0.01 chains/nm² (black). Center: a particle network, 17 kg/mol graft, 0.05 chains/nm² (red). Right: sheets of particles, 24 kg/mol graft, 0.1 chains/nm² (blue). (B) Steady shear data at 180 °C at a shear rate of 0.2/s. (C) Storage modulus data for the same three nanocomposites, also taken at 180 °C. Reproduced from ref 57.



Figure 10. In a "morphology" diagram we plot symbols whose size scale with the degree of reinforcement as characterized by the ratio (stress overshoot maximum value)/(plateau value). Other measures give qualitatively similar results. Only the well-dispersed sample yielded no stress maximum. Reproduced from ref 57.



Figure 11. Reinforcement percentage of the (a) elastic modulus, (b) yield stress, and (c) failure strain relative to the pure polymer depending on grafting density σ and grafted/matrix chain lengths ratio α . The loading of the silica core was 5 mass % in all the samples, and the morphologies of NP in these thin films are those reported in ref 56. Reproduced from ref 199.



Figure 12. Visualization of nanocomposites formed by TiO_2 grafted with PDMS in a PDMS matrix. Reproduced from ref 120.



Figure 3. Self-assembly of BCP-tethered AuNPs into hollow structures. (a–c) Assembly mechanism (a) and SEM images of the resulting vesicles (b) and tubules (c). (d) Product diagram of the self-assembly of HINPs into different structures: \triangle , vesicles; \bigcirc , tubules; \times , precipitates. (e) Plot of the interparticle spacing D_{Au} (\triangle) and $D_{Au}/2R_0$ (\bigcirc) of vesicular assemblies as functions of PS length. Reprinted from ref 23. Copyright 2012 American Chemical Society.

He J, Liu Y, Babu T, Wei Z, Nie Z Self-assembly of inorganic nanoparticle vesicles and tubules driven by tethered linear block copolymers. J. Am. Chem. Soc. **134** 11342–11345 (2012).

Huang J, Zhou J, Liu M Interphase in Polymer Nanocomposites JACS Au 2 280-291 (2022).



Figure 1. Formation and transfer mechanism of the interfacial phase in nanocomposites. In nanocomposites, the polymer chains can adsorb on the surface of nanoparticles due to various interactions, which greatly limit chain motion. The adsorbed chains form many "loop" structures, which provide effective sites for entanglement with the surrounding polymer chains. The interphase is formed by infiltration of the surrounding chain into the adsorbed chain. The relaxation of polymer chains in the bulk is influenced by the entanglement transfer of the interphase, which improves the macroscopic mechanical properties of nanocomposites.



 $h_{\rm ads}(t) = h_{t=0} + \Delta h (1 - e^{-t/\tau})$

Figure 2. Structure control and propagation distance of the interphase. (a) Effect of equilibration time on interphase thickness. The interphase thickness increases with an increase in heat treatment time and then tends to a plateau. (b) Control of interphase thickness by adjusting the adsorbed chain structure. The interphase thickness increases with an increase in the molecular weight of the polymer chain. Meanwhile, the interphase thickness can be changed by adjusting the adsorbed chain conformation. (c) Long-range effects of the interphase. Up to now, most literature has reported that the propagation distance is in the range of $3-11R_{\rm e}$.



Figure 3. Size effects of the interphase in nanocomposites. (a) Schematics of the different regimes for size effects of the interphase. (b) Effect of interparticle separation distance on the T_g values of nanocomposites. These data are gathered from refs 14 and 74–78. (c) Relaxation times of nanoparticles (τ) and the storage modulus (G') in the nanocomposites obtained determined at $\omega = 0.1$ rad/s. Reprinted with permission from refs 72 and 73. Copyright 2017 and 2018 American Physical Society.

(2)

 $d = d_{\rm NP} \left[\left(\frac{2}{\pi \phi_{\rm NP}} \right)^{1/3} - 1 \right]$

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Figure 4. Effects of the interphase spacing on nanocomposites. (a) Schematic diagram illustrating the interphase between the aligned nanosheets at different interlayer distances. The strength and modulus (b), plots of the diffraction vector (c), and curves of tan δ versus temperature (d) of nanocomposite films with the filling amount of nanofillers.



Figure 5. Design strategies of nanofiller structure inspired by natural products. (a) Alignment: tooth enamel and mother of pearl/nacre. Twisting: *Arapaima gigas* scale and conch shells. (b) Nanocomposites with binary combinations of nanofillers. Reprinted with permission from refs 8, 81, and 92. Copyright 2017 Wiley-VCH and 2016 Royal Society of Chemistry.

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Bailey EJ, Winey KI Dynamics of polymer segments, polymer chains, and nanoparticles in polymer nanocomposite melts: A review Prog. Polym. Sci. **105** 101242 (2020)



Fig. 1. Schematic to highlight the time- and length-scales of various dynamic processes in polymer nanocomposites (PNCs).



Fig. 2. Primary segmental relaxation times (α -process) of bulk 40 kg/mol P2VP as a function of inverse temperature. Shaded regions depict the approximate time scales and their corresponding temperature scale for five techniques: temperature-modulated differential scanning calorimetry (TMDSC), dynamic mechanical analysis (DMA), broadband dielectric spectroscopy (BDS), neutron spin echo (NSE), and quasi-elastic neutron scattering (QENS). Black line represents a VFT fit for TMDSC (red circle), BDS (blue circles), and QENS (green circles) measurements of neat P2VP [55]. Copyright 2019. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 3. Schematic showing polymer segmental dynamics as a function of distance from a single NP. The homogeneous model (left) assumes an average relaxation time throughout the polymer matrix. The core-shell model (center) spatially separates the polymer relaxations into a slower population adjacent to the NP and another bulk-like population away from the NP surface. The interfacial layer model (right) assumes a distribution of relaxation times that decreases smoothly from the NP surface into the matrix.



Fig. 4. Mean molecular relaxation time (τ_{Max}) as a function of inverse temperature for neat poly(2-vinylpyridine)(black squares) and P2VP segments in P2VP/SiO₂ PNCs ($\phi_{NP} = \sim 26 \text{ vol\%}$, blue). Relaxation times in the PNC are separated and plotted as interfacial relaxations (blue open diamonds) and bulk-like relaxations (blue filled diamonds) [65]. Copyright 2014.



Fig. 5. Schematic representation of the MW effect in PNCs with attractive NPpolymer interactions. (a) and (c) Nanoparticles in polymer solutions with free (green) and adsorbed (red) chains. (b) and (d) Polymer nanocomposites formed by solvent evaporation with free (green) and adsorbed (blue and red) polymers. For PNCs with low M_w, the bound chains are compact resulting in a similar BLL (bound loop layer) and DIL (dynamic interfacial layer) and overall slower segmental dynamics than PNCs with higher M_w with larger BLL than DIL [73]. Copyright 2016. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 6. Effect of NP size in P2VP PNCs with SiO₂ NPs (blue squares, $2R_{NP} = 25 \text{ nm}$) and octaaminophenyl polyhedral oligomeric silsesquioxane (OAPS) (red circles, $2R_{NP} = 1.8 \text{ nm}$) as a function of NP volume fraction. (a) Changes in glass transition temperature, $\Delta T_g = T_{g,PNC} - T_{g,bulk}$, (b) magnitude of the step in heat capacity from TMDSC, and (c) fragility [108]. Copyright 2017.

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Fig. 7. Segmental relaxation time for $\varepsilon = 0.1, 0.25, 0.5, 0.75, 1.0, 1.4$, and 2.0 as a function of distance from the NP surface. Inset shows surface segmental relaxation time (normalized to that of bulk) as a function of interaction strength [119]. Copyright 2016.



Fig. 8. Incoherent dynamic structure factor (top) and mean square displacement (bottom) of PEO in neat PEO (teal diamonds) and PEO-based PNCs composed of PMMA-coated SiO₂ (red triangles) and bare SiO₂ (black squares) at T=423 K and bare SiO₂ in PEO at T=443 K (green squares). All PNCs were filled with φ_{NP} = 17.6% (core only) [141]. Copyright 2016. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 9. (a) Normalized dynamic structure factor from NSE of PEP for a variety of NP concentrations ($\phi_{NP} = 0$, 0.18, 0.35, 0.5, and 0.6 from black squares to purple tilted-triangles and $2R_{NP} = 17$ nm). (b) Separation of apparent tube diameter, d_{app} , measured in (top) and contributions of polymer entanglements (d_{tube}) and geometric NP-induced entanglements (d_{geo}) [149]. Copyright 2011. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 10. General schematic of diffusion experiment using a mutual diffusion sample configuration.



Fig. 11. Master curve developed for a variety of PS-based PNC systems showing collapse of the tracer diffusion coefficient normalized to bulk as a function of the effective interparticle distance relative to the tracer polymer chain size. Filled and open symbols refer to grafted and bare NPs, respectively [182]. Copyright 2013.



Fig. 12. Temperature dependence of polymer diffusion showing more perturbed diffusion at higher temperatures. Measurements are for 532 kg/mol dPS diffusion into PS/SiO₂ PNCs (ϕ_{NP} = 0–50 vol%, 2R_{NP} = 28.5 nm, T_g^{PS} ~ 375 K) [188]. Copyright 2016.



Fig. 13. Diagram representing the effect of NP diameter and length relative to polymer R_g on observations of monotonic (open symbols) or non-monotonic (closed symbols) dependence of normalized tracer diffusion coefficient as a function of NP concentration, as schematically shown in the inset. Data is compiled from PNCs containing spherical SiO₂ (star symbols), CNTs (triangle symbols), and nanorods (square and circle symbols) [201]. Copyright 2014.



Fig. 14. Self-consistent generalized Langevin equation (SCGLE) predictions for repulsive NP diffusion relative to SE behavior in entangled polymer melts as a function of NP size, R_{NP} , relative to the tube diameter, d_{tube} , for N/N_e = 4 (black), 8 (red), and 16 (blue) [216]. Copyright 2015. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

SE = Stokes-Einstein



Fig. 15. Crossover from core shell diffusion ($D < D_{SE}$) to vehicle diffusion ($D > D_{SE}$) for OAPS diffusion in PPG as a function of molecular weight [246]. Copyright 2018.



Fig. 16. Comparison of relaxation times for poly(2-vinylpyridine) (P2VP) at various length-scales and attractive OAPS NPs as a function of P2VP molecular weight. The Rouse times of a Kuhn monomer (τ_0 , BDS) and P2VP reptation time (τ_{rep} , ERD) were measured on bulk P2VP. OAPS relaxation times (τ_{OAPS}) are calculated directly from RBS measurements. All measurements are made at 140 °C [109]. Copyright 2019.



Fig. 17. (a) Nanoparticle relaxation time as a function of q for PEG functionalized SiO_2 in PMMA of varying molecular weight. Solid line denotes superdiffusion (q^{-1}) and dashed line denotes Brownian diffusion (q^{-2}) . (b) NP velocity extracted as the slope of (a) as a function of entanglements per chain [159]. Copyright 2016.