

Supplementary Information

Bound polymer layer in nanocomposites

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I. Particle size analysis

The particles come in one of four sizes as reported by Nissan: the smallest particles are 10-15nm, followed by particles 17-23nm in diameter, then 40-50nm, and the largest particles are 70-100nm in diameter. The smallest particles were supplied in MEK only and the 17-23nm particles and the 70-100 nm particles were in IPA only. The 40-50nm particles were available in both solvents, and we used these to check for any effects on the solvent used. In order to create precise measurements of the bound layer thickness, a well-defined NP geometry is necessary. The size is reported by Nissan as a range, but an average size is required for bound layer thickness calculations both in DLS and using the TGA (discussed further onward). Therefore, a large number of TEM images were taken of the particles, and the diameters of several hundred particles were measured using the ImageJ software. This analysis was compared to similar measurements taken using DLS and the results are reported in Figure SS1 and Table SS1.

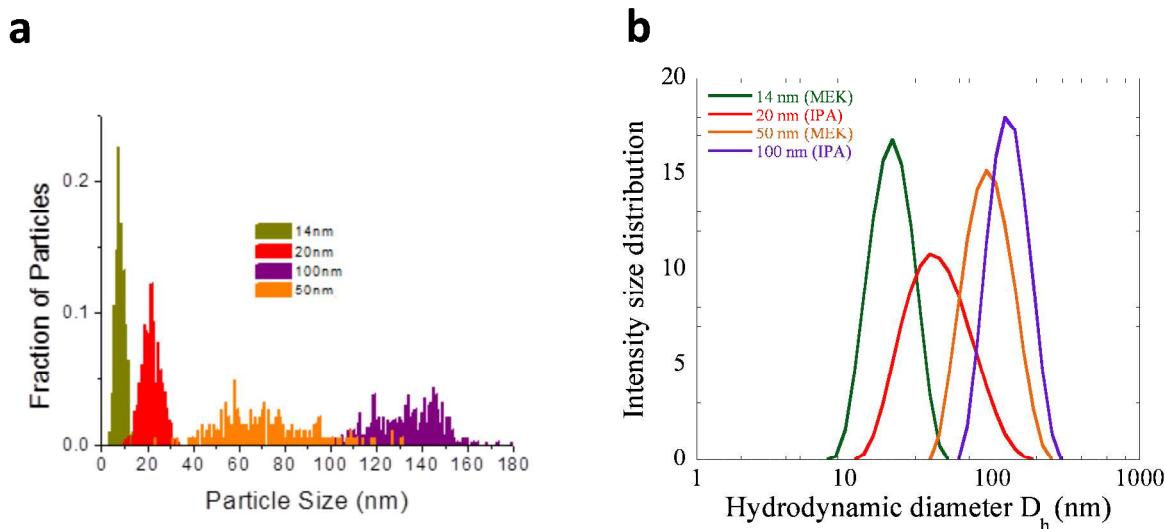


Figure SS1. Particle size distribution for the Nissan Chemical particle sizes as taken by image analysis of TEM micrographs (a) and using a DLS on 0.1%wt solutions of the particle (b).

Table SS1. Average NPs size according to the supplier and obtained by TEM analysis and DLS measurements.

Particles:	S (MEK)	M (IPA)	L (IPA)	L (MEK)	XL (IPA)
Size distribution given by the supplier Nissan Chemical (nm)	10-15	17-23	40-50		70-100
TEM Average diameter (nm)	8.5	22.5	70.9	56.0	134
DLS Average Diameter (nm)	21.7	39.6	73.9	87.4	114

II. Details on Sample Preparation

The sample preparation has been already detailed in reference [7] of the main text. Here we remind the reader of the main preparation steps. Particle solutions in MEK are prepared by adding 1 mL pyridine to 4 mL of the particle solution as manufactured. Particle solutions in IPA must be further diluted to prevent gel formation by combining 2 mL of the particle solution as supplied with 10 mL of IPA and 3 mL of pyridine (in that order). Various ratios of pyridine to solvent were tested and 4:1 was determined to be optimal. Thus, the relatively small amounts of pyridine added in these experiments serve simply to

prevent the initial bridging and quicken the process of sample preparation. Given enough time, the same well-dispersed particles will result regardless of addition of pyridine. For each nanocomposite to be prepared, 0.2 g of P2VP is dissolved in 4 mL of solvent, either MEK or IPA depending on which solution the particles are provided in. These prepared solutions are vortexed for 1 hour. The concentration of each solution is then measured by pipetting 100 μ L onto a tarred weighing paper, allowing the solvent to fully evaporate, and using the observed weight to calculate concentration. Based on the measured concentrations, appropriate volumes of both the particle solution and the polymer solution are combined such that 30% of the combined mass is silica and 70% is P2VP, except in the case of the 22nm particles, where 40% silica is used to promote full pellet formation. This combined solution of both particles and P2VP is again vortexed overnight, followed by one minute of sonication (2s sonicate, 1s rest). It is then poured into a Teflon coated petri dish and left in the fume hood to dry.

III. Transmission Electronic Microscopy (TEM)

After drying, a small section of the sample is selected to confirm the particle dispersion state using electron microscopy. The section is embedded in epoxy and cured at 80°C for 8 hours. It is then microtomed using a Leica UCT microtome into 60-100nm sections and placed on a formvar coated copper TEM grid. These sections are visualized using a JEOL JEM-100 CX transmission electron microscope (TEM).

IV. TGA procedure for bound layer measurements

To determine the bound layer thickness, the remainder of the sample is again dissolved in its respective solvent, either MEK or IPA. If the sample is to be annealed, then, it is placed in an oven under vacuum at 150°C before dissolving. This dissolved sample is vortexed overnight and then centrifuged at 13,000 rpm for 5 minutes. The particles form a pellet at the bottom of the centrifuge tube, and any bound P2VP is

incorporated into the pellet as well. The unbound P2VP remains in the supernatant. This washing process is repeated, to ensure removal of all unbound P2VP. It was experimentally determined that two washes is sufficient after observing a convergence of the bound layer thicknesses at two washes of samples that were washed between one and five times (Figure SS2). This was done for nanocomposites with particle weight fractions ranging from 16-86%. The resulting pellets are completely dried first in the fume hood overnight, then at 80°C under vacuum. Finally, the pellets are each burned in a thermogravimetric analyzer (TGA) in a heating sequence as follows: isothermal at 30.0°C for 2.0 minutes, temperature increase from 30 to 150°C at 20.0°C/min, isothermal at 150.0°C for 10.0 minutes (to confirm the absence of solvent), and a temperature increase from 150 to 1000°C at 10°C/min where the P2VP is expected to burn off at around 450°C. The silica does not burn off. Assuming that each particle and any bounded polymer conforms to a perfectly spherical geometry, and using the percentage of the pellet which was P2VP as determined by the TGA, the bound layer thickness is calculated. Since we do not know the exact density of the bound P2VP, we assume the same density as the bulk to calculate thickness.

Note that the particles are manufactured with a coating that prevents agglomeration. This coating may at least partially burn off during the TGA run. Since the Nissan particles are proprietary, information about the coating is not readily available. Therefore samples of pure particles of each size used were burned to determine what fraction of the particle weight is coating. Similarly, to account for the small amount of P2VP that does not burn off, TGA runs were performed on pure P2VP. The results were different for each particle size and solvent and are shown in Table 2. The fraction of the particle that is coating is directly used in every bound layer thickness calculation.

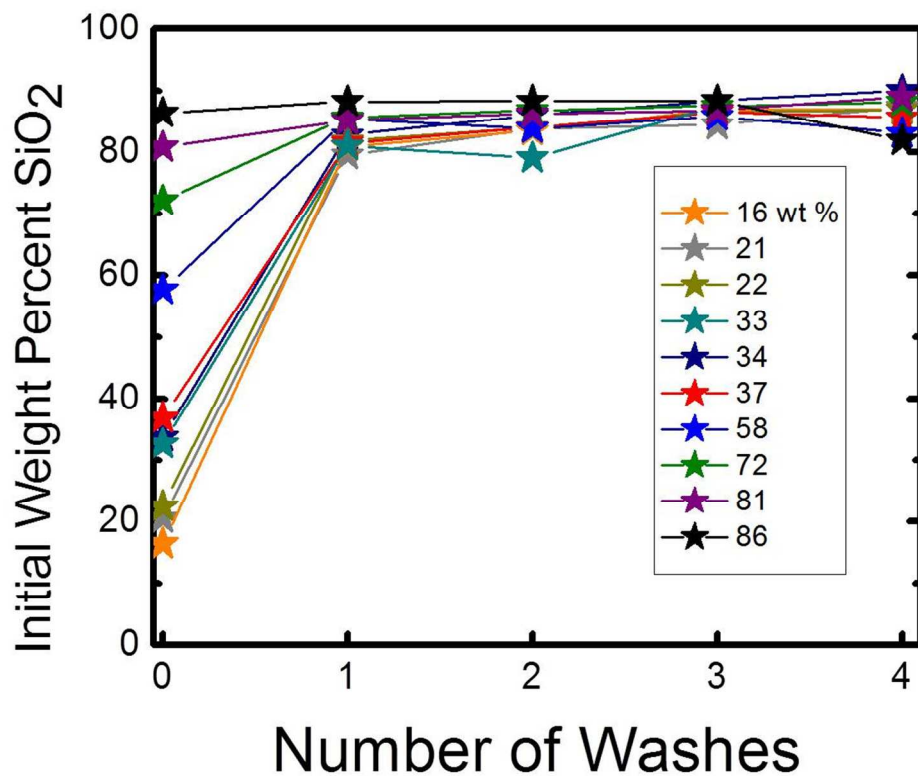


Figure SS2. Weight Percent SiO₂ as a function of the initial loading, and number of washes, of the nanocomposite. The bound layer achieved is largely independent of initial loading, up to a loading of 86% by weight..

Table SS2. Particle coating information

Particle Size (nm)	Solvent	Thickness of Coating (nm)	Fraction of ParticleThat is Coating
14	MEK	0.12 ± 0.03	0.022 ± 0.005
22	IPA	0.06 ± 0.01	0.008 ± 0.001
70	MEK	0.27 ± 0.02	0.0104 ± 0.0008
80	IPA	0.208 ± 0.03	0.008 ± 0.001
114	IPA	0.5055 ± 0.1	0.010 ± 0.002

V. Bound Layer Thickness Dependence on Particle Loading

In Figure SS2 we plot the fraction of silica in the pellet as a function of particle loading (the remainder of the pellet is adsorbed polymer). This is done for small size NPs. In the figure, we plot the fraction of silica in the freshly prepared composite, and after four different wash cycles. Ten samples ranging from 16-86% silica by weight were studied in order to determine the effect of weight percent on bound layer thickness. For small weight fractions, we do not expect to see a difference in the calculated bound layer thickness, as there is plenty of polymer to form a full equilibrium bound layer. As the weight fraction is increased, the total amount of polymer available per particle should decrease, and at some point, there may no longer be enough to fully distribute itself to the NPs. Such a scenario would presumably lead to a decrease in the bound layer. Apparently, even at the highest NP loadings studied, this threshold is not reached. The thickness of the bound layer was essentially invariant. Even at a loading of 86 wt % (which translates to 76% volume) the particles are still able to form a full (or very close to full) layer. Note, however, that to ensure that the amount of polymer would not limit the bound layer size, all experiments were done with particles that were 40% or less by weight of silica particles. TEMs of 14nm diameter samples at many different weight percents showed uniform dispersion.

VI. Bound Layer Thickness as a Function of Annealing

We consider in further detail the effect of annealing at high temperatures on bound layer thickness for polymer nanocomposites. The purpose of annealing is to achieve a full, equilibrium bound layer. In order to determine the appropriate annealing time, the bound layer thicknesses of the second largest particle size, annealed from 6 hours to 8 days were compared. The large particles were chosen as they are approximately the same size and they come in both of the studied solvents and thus facilitate a solvent comparison. The results in Figure SS3 show an increase in bound layer thickness from 6 hours

up to 3 days. Beyond 3 days of annealing, the thickness remains roughly constant with perhaps a slight decrease in thickness at the longest time of 8 days (possibly indicating degradation). The results are consistent for both IPA and MEK, although in all cases the IPA particles have a thinner bound layer, expected given the smaller particle size. However, a thinner bound layer in IPA was also achieved when particles of the exact same size were washed in the two different solvents (results not shown). Based on these results, as a precaution, all samples were washed with MEK, even those prepared in IPA. Five days is also apparently the optimal annealing time for the formation of a bound layer. Apparently, in solution, the chains do not fully adsorb, presumably because of competition with the solvents. Pyridine is used as a co-solvent and it is a strong Lewis base. In solution, it competes with the P2VP for surface sites, therefore annealing is crucial to allow a full bound layer formation.

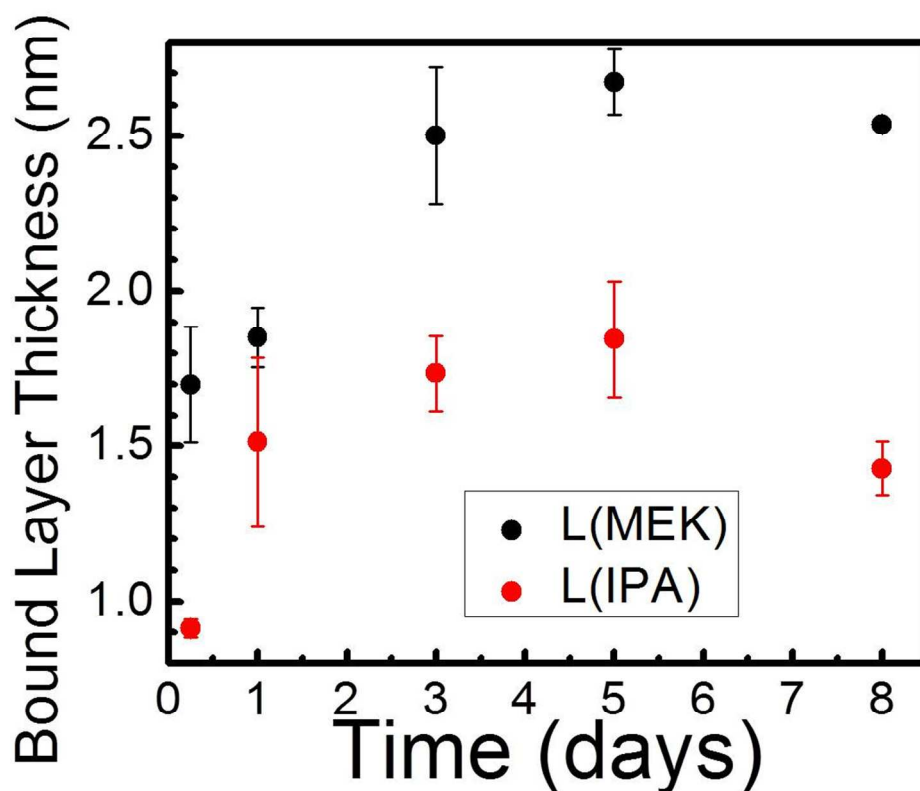


Figure SS3. Bound layer thickness as a function of annealing time for large Nissan particles in both IPA (red) and MEK (black).

VII. Bound Layer Thickness in solution

The DLS experiments have been performed on a Zetasizer NanoZS (Malvern Instrument) operating in backscattering mode at an angle of 173° and at a temperature of 25°C. For these experiments we prepared very dilute silica/P2VP/solvent (in MEK or IPA) solution (0.1%wt in silica) to avoid any aggregation induced by polymer bridging. The P2VP concentration is fixed at $c=1.7$ g/L and the viscosity of the solution is kept equal to the pure solvent. Then, the hydrodynamic bound layer thickness δ_h is obtained by subtracting the average diameter of bare silica from the average size measured in the presence of P2VP and dividing the result by a factor 2. The hydrodynamic diameter is determined by fitting our time auto-correlation function $g^{(2)}-1$ using the CONTIN procedure (the error bar on the diameter is +/- 2%).

VIII. Interaction pair potential calculation

To distract the effective interaction potential between NPs from the experimental TEM images, the radially averaged autocorrelation function $C(r)$ is first calculated using the image processing software ImageJ. $C(r)$ basically calculates the two-point correlation of the pixels of an image as a function of distance and gives information about the typical feature size in an image. The initial slope, first zero and first minimum include information on particle and hole sizes; the first side maximum of the autocorrelation gives the typical distance between two particles. The next step is to set up Metropolis Monte Carlo simulations with the same number of particles and box size dimensions as in the TEM image. The NP size distribution in the simulations is also determined from experiments. The Derjaguin approximation is employed to describe the interacting force between two spherical particles i and j

$$F_{ij}(r) = \begin{cases} 0, & r > 2L \\ \sigma^{eff} W(r), & \sigma_{ij} < r \leq 2L \end{cases} \quad (S1)$$

where $\frac{1}{\sigma_{eff}} \equiv \frac{1}{\sigma_i} + \frac{1}{\sigma_j}$ is the effective diameter and $W(r)$ is interacting energy per surface area between two planar walls. We assume that the surface of the two particles are strongly adsorbed with polymer chains. $W(r)$ is thus represented by the Alexander-de Gennes equation [1] for the interaction potential between two brush bearing planar walls:

$$\beta W(r) = - \int_{2L}^r a \left[\left(\frac{r'}{2L} \right)^{-9/4} - \left(\frac{r'}{2L} \right)^{3/4} \right] dr' \quad (S2)$$

where a is a parameter depending on the grafting density and L is the brush layer thickness. The pair interaction potential $U_{ij}(r)$ used in the simulation for a given particle size is derived by integrating Equation (S2). A series of Monte Carlo simulations are performed for each system represented by one TEM image through adjusting a and L as fitting parameters. Snapshots are collected during each simulation and then passed to ImageJ to calculate an averaged $C(r)$. The a and L are varied until the $C(r)$ from simulations matches that of TEM images. The final values of the two fitting parameters are shown in Table SS3. As an example, Figure SS4 shows a binary TEM image from experiments (left) and a snapshot from the corresponding simulations when a matching $C(r)$ is achieved (Right).

Table SS3. Interaction potential fitting parameters

Particle Size Simulation (DLS)	L (σ)	a	h (nm)
14 σ (21.7nm)	10	0.01	3.75
20 σ (40 nm)	20	0.015	7.50
50 σ (87.4 nm)	25	0.015	9.38

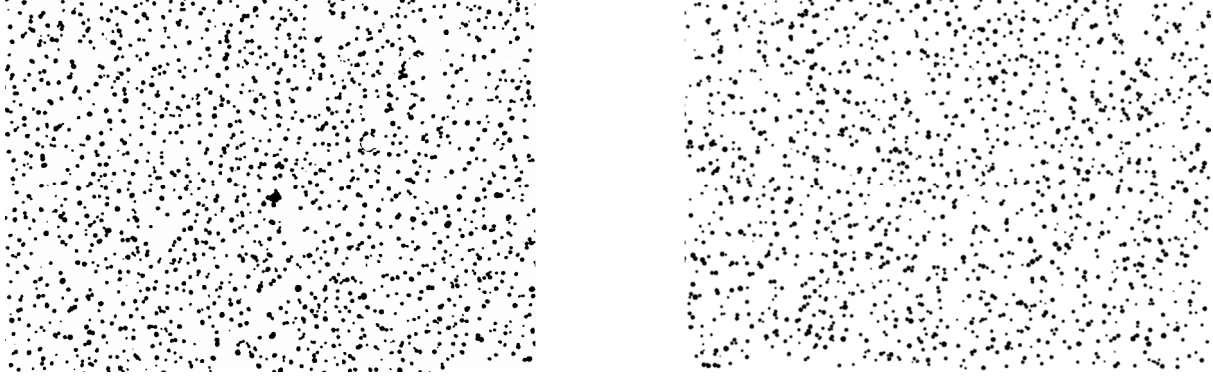


Figure SS4. (Left) Binary TEM image for 20nm nanoparticles (termed **M** in Table SS1) at a loading of 10%. (Right) Simulation snapshot for the system shown in the left.

After the effective interaction is obtained, the adsorbed surface layer thickness h is estimated by calculating the first moment of a parabolic density profile $\rho(r)$ that is assumed based a brush structure [2] with $\rho(0) = 1$ and $\rho(L) = 0$, i.e.,

$$h = \frac{\int_0^L r \rho(r) dr}{\int_0^L \rho(r) dr} = \frac{3}{8} L \quad (\text{S3})$$

REFERENCES

- [1] de Gennes, P.G. *Advances in Colloid and Interfaces Science* **1987**, 27, 189-209.
- [2] Milner, S.T.; Witten, T.A.; Cates, M.E. *Macromolecules* **1988**, 21, 2610-2619.