

Bound Polymer Layer in Nanocomposites

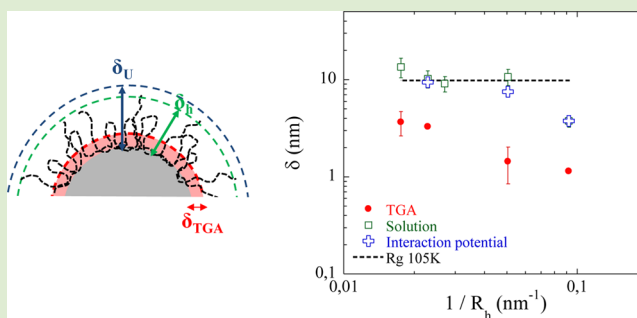
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Supporting Information

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.



Polymer nanocomposites (PNC), produced by adding nanoparticles (NPs) to polymer melts, frequently display significantly improved thermomechanical properties relative to the pure polymer. It is currently thought that attractive interactions between the NPs and the polymer are necessary to achieve these property improvements. These attractions strongly slow down chain mobility close to the surface, creating an effectively irreversibly bound polymer layer.¹ (In some cases, when the attractions are weaker or for short chains, the bound layer can also be at equilibrium.) Over the last century, there have been many experimental^{2–8} and simulation^{9–11} attempts to quantify the total amount and extent of this bound polymer. We describe a popular method used to obtain this thickness. One takes a PNC and strips away any polymer that is not strongly adsorbed on the NPs. Thermogravimetric analysis (TGA), or a comparable technique, yields the amount of adsorbed polymer. The bound layer thickness is estimated by assuming that the polymer layer has a density equal to its melt value. Most consensus estimates are that the bound layer thickness is 1–4 nm, with a weak dependence on NP size.^{2–11}

A different approach to estimating an interfacial layer thickness is based on studies of polymer adsorption onto flat surfaces from solution. Granick, Schweizer, and co-workers suggest that the presence of an attractive surface–polymer interface creates an essentially irreversibly adsorbed layer with thicknesses comparable to the radius of gyration R_g of the chains in question.¹²

These two sets of apparently disparate results motivate the current work. Why does the TGA predict such small bound layer thicknesses? On the other hand, why do polymer

adsorption data on flat surfaces yield such large adsorbed layer thicknesses?¹² Is there any means to reconcile these factors of 3–5 differences in layer thicknesses? What is the influence of NP size? We critically investigate these questions by coupling three different methods: thermogravimetric analysis (TGA), dynamic light scattering (DLS), and a quantitative analysis of transmission electronic microscopy (TEM) images of NP dispersion in a polymer matrix.

We study PNCs of silica NPs and poly-2-vinylpyridine (P2VP). The silica NPs of five different diameters (Nissan Chemicals) were dispersed in either methylethylketone (MEK) or isopropanol (IPA), 22 nm (MEK), 40 nm (IPA), 87.4–73.9 nm (MEK or IPA), and 114 nm (IPA). These DLS-determined NP diameters are substantiated by TEM image analysis (Supporting Information (SI), Figure SS1). In all future references, we employ the DLS determined sizes. Eight different P2VP molecular weights (Polymer Source), M_w 2.4, 5.4, 14.7, 54, 105, 302, 554, and 940 kg/mol (K) with a polydispersity index (PDI) of 1.14, 1.07, 1.05, 1.04, 1.08, 1.09, 1.11, and 1.10, respectively, were used. The entanglement molecular weight, M_e , for P2VP is 27 kg/mol ($N_e = 257$), and the Kuhn length is estimated to be ~ 0.6 nm. The sample processing is detailed in the SI (see also, ref 7). The favorable interaction between the P2VP and the silica (the estimated adhesion energy is -350 mJ/m²¹³) allows the polymers to

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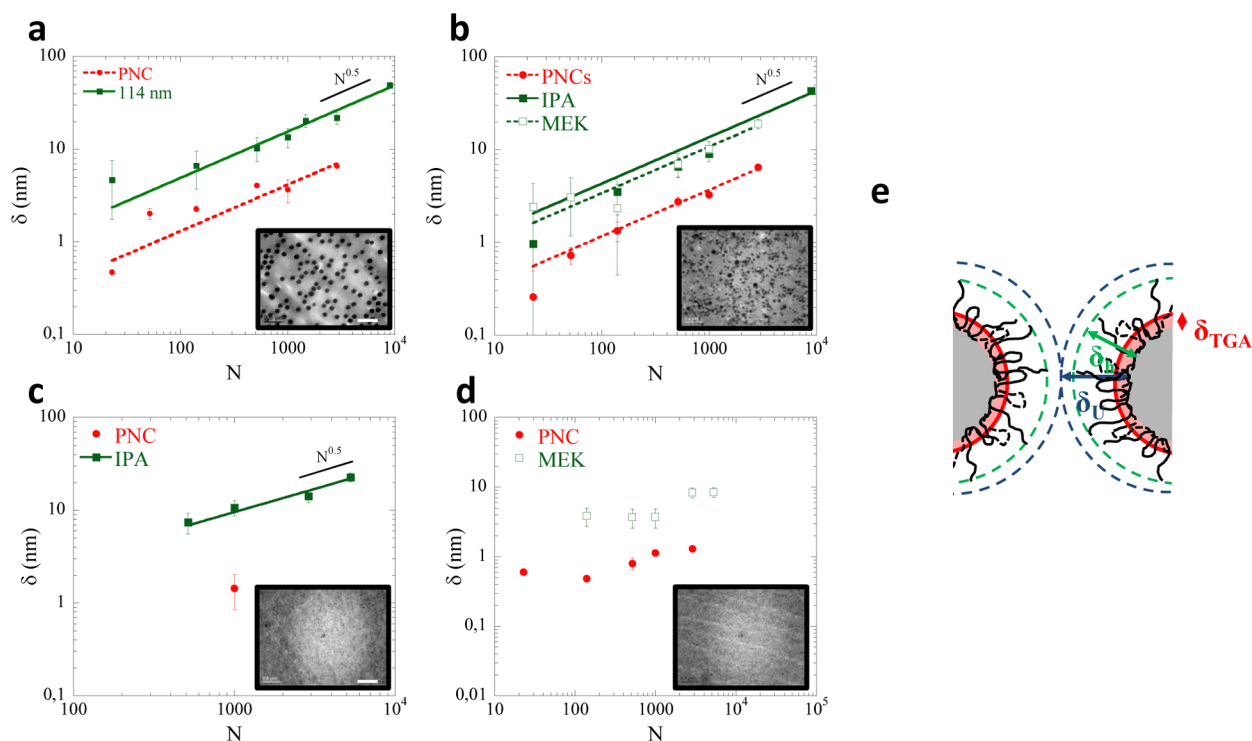


Figure 1. Bound layer thicknesses δ as a function of P2VP chain length N (or degree of polymerization) for (a) 114 nm, (b) 73.9 nm (IPA)–87.4 nm (MEK), (c) 40 nm, (d) 22 nm silica NPs. (The NP diameters were determined by DLS.) The red circles are the thicknesses determined in PNCs using TGA and the green squares are the thicknesses determined in θ solvent using DLS (full symbol, IPA; empty symbol, MEK). The continuous and dash lines scale as $N^{0.5 \pm 0.05}$. Inset: TEM images for 105K P2VP PNCs filled at 30 wt %, showing the good NPs dispersion (scale bar: 0.5 μm). (e) Sketch of polymer layer on silica NPs. The red area represents the thickness δ_{TGA} measured in PNCs by TGA assuming a uniform density corresponding to a dense melt to describe the layer. The green dash line schematically represents the hydrodynamic thickness δ_h measured in θ solvent by DLS, mainly determined by tails. The blue dash line represents the thickness δ_U determined by measuring the interaction potential between NPs via TEM analysis. We find $\delta_U \approx \delta_h$.

form a bound layer,⁷ which also ensures a random NP dispersion (Figure 1, TEM images for 105K P2VP with 30 mass % NP).

We first conducted TGA measurements in the same spirit as many previous attempts to characterize the bound layer (see experimental details in the SI). We use the P2VP bound layer mass determined by TGA and assume a core–shell spherical geometry (red area in Figure 1e) where the bound layer has the same density as the bulk polymer. The effect of P2VP chain length (or degree of polymerization) N on bound layer thickness δ_{TGA} for 22, 87.4, and 114 nm silica in PNCs is presented in Figure 1. At a given N , the δ_{TGA} increases with increasing NP size (Figure 3).¹⁴ $\delta_{TGA} \sim N^{0.5 \pm 0.05}$ for 114 and 87.4 nm NPs (i.e., when $R_{NP} > R_{g,P2VP}$). The 22 nm data has five points with a weak dependence on molecular weight. We suspect that these measurements have more uncertainty than for the larger NPs because of the smaller amount of polymer adsorbed, coupled to difficulties in getting a full separation of the NPs from the solvent by centrifugation. We only studied one experimental point for the 40 nm particles simply to establish that the TGA results for this particle size were consistent with the other NP sizes. In this case, $\delta_{TGA} \sim 1$ nm, which is in line with a previous DSC study (~ 1.4 nm).⁷

Theoretical calculations predict that $\delta \sim N^{1/2}$.¹⁴ To understand this result, we note that a melt chain, of size R_g , makes $N^{1/2}$ contacts with a flat surface, on average. Thus, the number of chains that adsorb at full coverage scales as $N^{-1/2}$. Because each chain has N monomers, the total number of monomers in the bound layer and, hence, the bound layer

thickness, scales as $NN^{-1/2} \sim N^{1/2}$. This scaling is in reasonable agreement with our results for the larger NP sizes, while the smallest NP data are too noisy to critically comment on this issue.

In deriving the TGA brush height scaling, we implicitly assumed that the bound layer height must scale as the R_g of the chains. Theoretical work¹² for polymers adsorbed onto a flat surface show that the adsorbed layer height must be $R_g/3^{1/2}$. We therefore expect that the bound layer dimensions that result should be roughly equal to the R_g of the chains; instead, we find TGA-determined sizes that are a factor of at least 3 times too small (Figure 3). We therefore believe that these results are an underestimate of the true bound layer thickness and that the weakest assumption is that the polymer layer assumes a uniform density equal to the one of the melt.¹⁵ We expect on reasonable physical grounds that, in the PNC, unadsorbed (or free) chains add to the density provided by the adsorbed chains, $\rho_{\text{bound}} + \rho_{\text{free}} = \rho_{\text{melt}}$. To assume that $\rho_{\text{bound}} = \rho_{\text{melt}}$ likely causes an underestimate of the bound layer thickness.

To fix this crucial underpinning assumption requires that we measure bound polymer layers in the polymer nanocomposites. This in situ measurement is hard due to the relatively small contrast between the adsorbed layers and the bulk polymer.⁵ While this contrast could be accentuated by the use of labeling methods and small angle neutron scattering, we used an indirect approach instead. As detailed in the SI, we used ~ 100 nm thick slices of 105K PNCs and studied them using TEM. We then computed the correlation function, $C(r)$, from these images. In all cases, the initial r dependence of the $C(r)$ can be

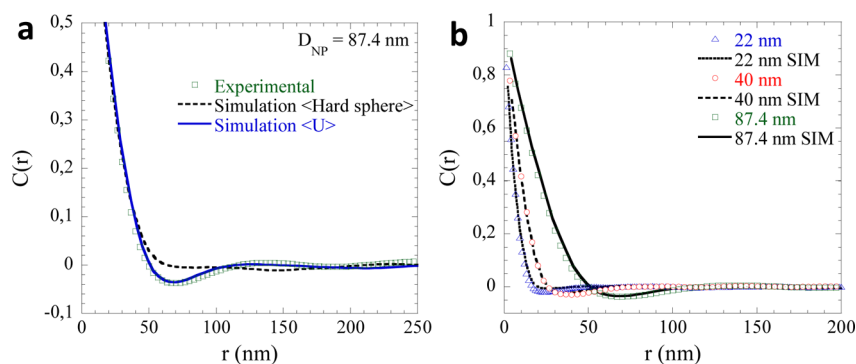


Figure 2. (a) Correlation functions $C(r)$ for 87.4 nm silica size in 105K P2VP at 10%wt of silica. The lines represent the fit from a hard sphere description (black dash line) and using an additional repulsive contribution in the potential (blue continuous line). (b) Correlation functions $C(r)$ for 22, 40, and 87.4 nm silica size in 105K P2VP at 10%wt. The black lines represent the fits.

reproduced by the known NP size distributions while assuming that the NPs themselves are spatially well dispersed. Thus, we numerically verify the visual finding that the NPs are not agglomerated (Figure 1 insets).

However, this random distribution model misses important elements of the longer ranged behavior of $C(r)$, especially its negative values at intermediate r . Figure 2a shows that the $C(r)$ from experimental TEM images cannot be reproduced with a pure hard sphere potential (black dash line); rather, an interaction pair potential derived from the Alexander-deGennes model for grafted chains on a flat surface¹⁵ gives a very nice agreement with the experiment $C(r)$ (blue continuous line). It must be emphasized here that there is no one unique means to fit these experimental data and that other empirical forms for the inter-NP potential are also able to describe the TEM data. Regardless of this nonuniqueness, the thickness dependence of the bound layer remains unchanged, reiterating the robustness of the conclusions derived (Figure 3).

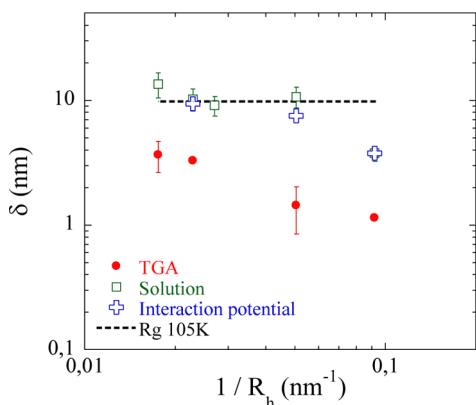


Figure 3. NP size dependence of the bound layer thickness δ for 105K P2VP in PNCs by TGA (red circles), in θ solvent (green squares) and by TEM analysis (blue cross) as a function of $1/R_h$, where R_h is the hydrodynamic radius of the nanoparticle.

We applied the same procedure for different silica sizes (Figure 2b) and convert this potential into an adsorbed surface layer thickness δ_U by calculating the first moment of the parabolic density profile $\rho(r)$ that is assumed based on a brush structure (see details in SI). As shown in Figure 3, these estimates of the bound layer thickness are ~ 3 – 5 times larger than the TGA estimates.⁵

The results obtained above from the PNC are indirect in that they are obtained from an effective inter-NP interaction potential used to describe the experimental $C(r)$. In addition to the uniqueness issue discussed above, there is no guarantee that these results can be attributed to a bound polymer layer only, and other effects such as the presence of surface charge could be crucial. To, thus, independently obtain an estimate of the bound layer, we used DLS for particles mixed with polymer in dilute solution in MEK or IPA. Both are θ solvents in which the P2VP conformation should not be swollen relative to the one in a polymer melt. The hydrodynamic bound layer thickness δ_h is obtained by subtracting the average diameter of the bare silica from the average size measured in the presence of P2VP. The result is then divided by a factor 2 (the error bar on the diameter is $\pm 2\%$). Figure 1 shows that δ_h is thicker than the TGA estimate by around a factor 5, but surprisingly it scales as $N^{0.5}$ within uncertainties. According to the Guiselin model¹⁴ for a bound layer with mass $a^{-2}N^{1/2}$ (as found in the TGA) the spatial extent in solution should scale as $N^{3/4}$. However, it has also been demonstrated that an adsorbed layer has a complex structure and is composed of two regions,^{16–18} one close to the surface where loops dominate and another one far from the surface rich with tails. The scaling of the tails is $N^{1/2}$,¹⁸ which is consistent with our own results and other, indirect estimates derived from PNC viscosity experiments by Jiang and Zukoski.⁵

Finally, we plot the bound layer thicknesses obtained with the three methods as a function of NP size (Figure 3 shows the results for 105K P2VP). It is apparent that the bound layer thickness from both DLS and TEM increases with increasing NP size. However, these values tend to a plateau value close to R_g in the large NP limit. Note that the TGA results show a similar plateau for large NP, but these estimates are a factor of 3–5 smaller than the other two methods. Second, the thicknesses derived from DLS and TEM match very well implying that the interaction between NPs in dry PNCs comes from the existence of bound polymer layers at the NP surface.

Here we reiterate that the TEM results were derived by an indirect technique, namely the fitting of TEM micrographs with an assumed interaction potential. It is well-known that such “inverse” calculations are difficult and nonunique, and so we emphasize that a certain degree of caution needs to be exercised in interpreting these numbers. While the DLS measurements apparently verify these TEM results, they were conducted in solvent, and hence, these are not equivalent to the melt matrices relevant to the PNC.

Our most important conclusion is that the bound layer thickness derived from DLS and TEM are substantially larger than those obtained from TGA measurements. Clearly, the effects of NP surfaces on polymer properties propagate to much larger distances than previously thought. The consequences of this statement on the properties of nanocomposites will be pursued in our laboratories.

■ ASSOCIATED CONTENT

📄 Supporting Information

Size analysis, sample preparation, TGA procedure, DLS measurements, TEM analysis, and interaction pair potential calculation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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