

PRF Grant Number: 57405-ND-7

Grant Title: Influence of Strongly Attractive Polymer-Substrate Interactions on Polymer Conformations and Chain Dynamics under Rigid Confinement

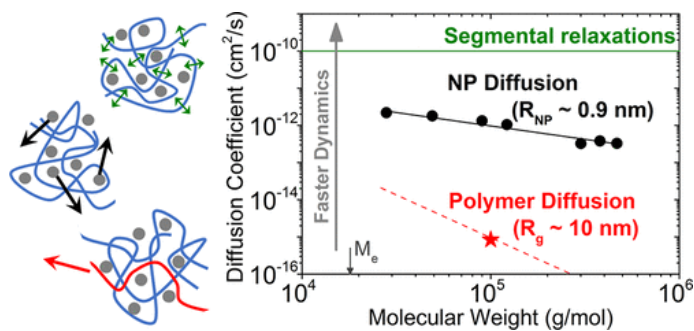
Principal Investigator: Dr. Karen I. Winey

PI Affiliation: Department of Materials Science and Engineering, University of Pennsylvania

Synopsis: A stable nanoparticle dispersion within polymer nanocomposites often relies on strong adsorption of the polymer onto the nanoparticle surface. In a new direction of research, we are exploring the conformation and the multiscale dynamics of polymers strongly adsorbed to nanoparticles. So far this grant has produced one published paper (*Macromolecules*), one submitted manuscript, and two manuscripts in preparation.

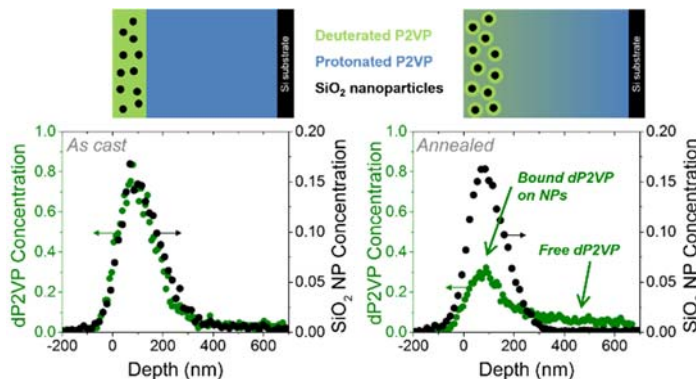
Multiscale Dynamics of Small, Attractive Nanoparticles and Entangled Polymers in Polymer Nanocomposites:

Polymer segmental dynamics, center-of-mass chain diffusion, and nanoparticle (NP) diffusion are directly measured in a series of polymer nanocomposites (PNC) composed of very small (radius ≈ 0.9 nm) octa(aminophenyl) polyhedral oligomeric silsesquioxane (OAPS) NPs and poly(2-vinylpyridine) (P2VP) of varying molecular weight. With increasing OAPS concentration, both the segment reorientational relaxation rate (measured by dielectric spectroscopy) and polymer chain center-of-mass diffusion coefficient (measured by elastic recoil detection) are substantially reduced, with reductions relative to bulk reaching $\sim 80\%$ and $\sim 60\%$, respectively, at 25 vol % OAPS. This commensurate slowing of both the segmental relaxation and chain diffusion process is fundamentally different than the case of PNCs composed of larger, immobile nanoparticles, where the motion of most segments remains relatively unaltered even though chain diffusion is significantly reduced. Next, using Rutherford backscattering spectrometry to probe the NP diffusion process, we find that small OAPS NPs diffuse anomalously fast in these P2VP-based PNCs, reaching diffusivities 10 – 10000 times faster than predicted by the Stokes–Einstein relation assuming the melt zero-shear viscosity. The OAPS diffusion coefficients are found to scale very weakly with molecular weight, $M_w - 0.7 \pm 0.1$, and our analysis shows that this characteristic OAPS diffusion rate occurs on intermediate microscopic time scales, lying between the Rouse time of a Kuhn monomer τ_0 and the Rouse time of an entanglement strand τ_e . Our findings suggest that transport of these very small, attractive nanoparticles through well-entangled polymer melts is consistent with the recently reported vehicle mechanism of nanoparticle diffusion. The paper appeared in *Macromolecules* 2019, 52, 5, 2181-2188.



Characterizing the Areal Density and Desorption Kinetics of Physically Adsorbed Polymer in Polymer Nanocomposite Melts:

The interfacial region between nanoparticles (NPs) and polymers in polymer nanocomposites (PNCs) underlie enhanced properties and the temporal stability of these bound polymer layers is necessary for extended control on PNC performance. Using ion scattering techniques and poly(2-vinyl pyridine) (P2VP) mixed with 26-nm silica nanoparticles (NPs), we investigate the lifetime of the bound polymer layer by separating and directly measuring the fraction of free polymer and polymer adsorbed to attractive NPs entirely in the melt state. By annealing thin PNC films deposited on bulk polymer matrices, free polymer from the PNC rapidly diffuses into the underlying matrix while the spontaneously-formed bound polymer in the melt remains with the slower NPs. By correlating the fraction of bound chains with the NP surface area, a bound layer thickness of $\sim R_g$ is observed in the melt. The calculated average NP surface area occupied by adsorbed chains in the melt is much smaller than predicted for an isolated chain or measured in a NP-polymer solution. The bound polymer fraction decreases as a function of annealing time and decreases more rapidly at higher temperatures and for lower molecular weights. This work demonstrates that ion scattering methods can



quantitatively measure the chain-scale structure and dynamics of polymers bound to NPs in the melt state. This new information provides fundamental insights and enables the design of PNCs with greater thermal stability during fabrication and use. This manuscript is under review at *Macromolecules*.

Dynamics of Polymer Segments, Polymer Chains, and Nanoparticles in Polymer Nanocomposites: A Review:

This invited review for *Progress in Polymer Science* will be submitted later this month. In the course of work on strongly attractive systems, we have encountered a variety of experimental and computation methods and results and this review is an effort to sort through the literature to identify the most reliable findings and the most pressing questions.

Creep Attenuation in Glassy Polymer Nanocomposites with Variable Chain-Particle Interactions: Here we examine the effects of nanoparticle size, concentration, and polymer-particle interactions on the viscoelastic creep properties of polymer nanocomposites. The nanocomposite systems are comprised of glassy thermoplastic polymers (polystyrene (PS) or poly(2-vinylpyridine) (P2VP)) and spherical silica nanoparticles. The particle polymer interaction strength is controlled by functionalizing the surface of the nanoparticles with trimethoxyphenylsilane to achieve a more neutral surface compared to the bare silica surface. By combining the bare and functionalized nanoparticles with PS and P2VP we create a range of polymer-particle interaction strengths, with P2VP-bare silica as the most attractive and PS-phenyl as the most neutral systems.

The viscoelastic creep behavior of the nanocomposite systems was measured using an accelerated dynamic mechanical analysis (DMA) testing method and the results were correlated with the equilibrium nanoparticle morphologies, observed using transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS). Significant differences in dispersion were observed between the nanoparticle systems, namely much worse dispersion of the phenyl-capped nanoparticles in PS compared to the bare nanoparticles in P2VP. Despite the observed morphological differences, caused by variations in interfacial interaction and nanoparticle size, the change in mechanical properties (including creep onset time and the relative reinforcement) was found to evolve predominantly as a function of nanoparticle concentration (**Figure 1**). This manuscript is in preparation.

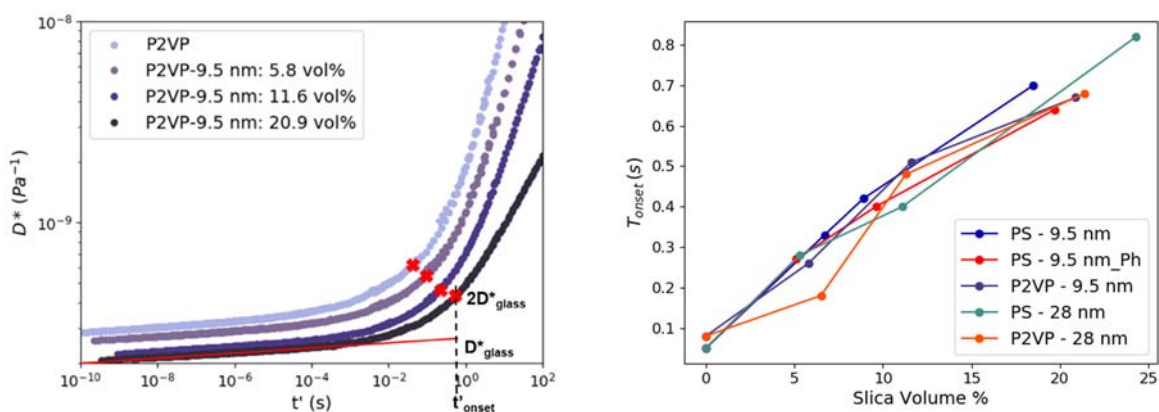


Figure 1. (left) Dynamic creep compliance (D^*) curves for P2VP-bare silica nanocomposites showing increasing stiffness and creep onset time with increasing particle loading. (right) a plot of the creep onset time as a function of silica nanoparticle volume fraction. The change in creep onset time is directly related to the particle volume fraction and not affected by the polymer-particle interaction strength.

Impact on my career and that of the students: Our ACS-PRF-funded research on polymer nanocomposites with strong attractions between the thermoplastic and the nanoparticles has attracted the attention of a corporate partner as they develop new polymer-based materials for infrastructure applications. Scientific interactions with industrial scientists provide invaluable context for our fundamental studies and various professional development opportunities for my research group.

November 20, 2019