

**BEHAVIOR OF GRAFTED POLYMERS ON
NANOFILLERS AND THEIR INFLUENCE ON
POLYMER NANOCOMPOSITE PROPERTIES**

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ABSTRACT

Polymer nanocomposites continue to receive wide-spread acclaim for their potential to improve composite materials beyond conventional macroscale fillers. The improvement lies both in the altered properties of the particle itself and in the interaction region surrounding the filler. As the surface area of the filler increases, a greater volume fraction of this interphase region is present in the composite.

However, simply minimizing the particle size to maximize surface area introduces additional problems; the larger specific surface area promotes aggregation to reduce the surface energy. Since the composite's properties are largely tied to the morphology, aggregation prevents control over the dispersion state of the filler, and thus the properties. Therefore, disaggregation and morphology control are vital to achieving designable nanocomposites.

To accomplish both tasks, this thesis focuses on the behavior of grafted polymer coatings on nanoparticles and their influence on the macroscopic properties. Grafted chains play an integral role in both morphology control and reinforcement.

To investigate the behavior of polymer brushes on nanoparticles, polystyrene was grafted on 15 *nm* silica particles at varying graft densities and molecular weights. Dynamic light scattering studies in dilute solution were performed to obtain the brush height as a function of both graft density and molecular weight. Three distinct regimes of behavior exist, the "mushroom", the semi-dilute polymer brush (SDPB), and the concentrated polymer brush (CPB) regimes. In the CPB regime, which is an extraordinary configuration of highly-stretched chains on densely grafted surfaces, the brush height h was found to scale as $h \propto N^{4/5}$, where N is the degree of polymerization. This result is contrary to the observed scaling of the CPB in flat interface systems, where $h \propto N^1$.

To explore the behavior of grafted chains in the melt, molecular dynamics simulations were performed on grafted nanoparticles grafted with varying amounts of polymer chains at different curvatures. Particles as small as 15 monomers in size were found to already be in the large particle limit, a result that has many

implications regarding the dispersibility of grafted fillers in composites. At low graft densities, melt chains were found to form entanglements with the brush all the way to the particle surface, implying the particle is not effectively screened by the grafted chains.

The mechanical properties of these grafted silica composites were studied as a function of matrix polymer fraction. As more matrix polymer is introduced, the dominant contribution to the behavior shifts from the grafted chains to the matrix chains. This elucidates the role of grafted chains on the mechanical properties of grafted nanoparticle composites. As the graft density is increased, the wettability of grafted chains was shown to decrease, causing fewer entanglements between grafted chains and matrix chains, resulting in poorer reinforcement.

Interesting behavior was observed at low graft densities; a pronounced shape memory effect occurred at high particle concentrations. It is proposed that the grafted chains entangle with adjacent grafted chains, forming a three-dimensional network of entangled brushes attached to silica cores. This structure effectively forms "cross-links" as in elastomeric systems, giving an entropic restorative force to stretched chains. Thus, above T_g , when chains have a higher degree of mobility, the composites can be stretched to over 800%. When cooled to below T_g , they retain the deformed geometry. Upon reheating above T_g , the composite is restored to its original dimensions.

This work has identified means of improving theoretical models to better guide future experiments and lead to predictability in polymer composite design. Grafted chains have the demonstrated ability to control the morphology and reinforcement in polymer composites. The behavior of grafted chains were shown to demonstrate drastically different properties from their bulk polymer counterparts.