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## **Optimization of Polymer Filler Materials**

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# Optimization of Polymer Filler Materials

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## Abstract

Filled-polymers are the most common organic-based materials used through out the world. However, the addition of fillers to polymer mixtures is an empirical procedure. The manufacture of neutron generators and electronic packages are but two of a number of processes deemed crucial to Sandia's mission that require the careful tailoring of a mixture of filler and polymer fluids. A powerful, novel approach designed to optimize the properties of this composite mixture was investigated. In particular, we looked at the need for the highest possible filler fraction with the lowest viscosity as dictated by the processing requirements. Computational modeling was an ideal tool for this task as it allows one to reliably determine the general trends needed to guide the mixture's design while minimizing the number of costly experiments. The idea is based on the following step-wise approach involving validation experiments and modeling. From our polymer fluids theory (PRISM) we determined the effective solvation potential acting between two-interacting filler particles. These potentials can be used as input to traditional Molecular Dynamics simulations of multiparticle systems to determine the viscosity. In determining the filler-particle size distribution that will optimize the composite's properties we built on our recent discovery that packing properties of polydisperse systems are almost entirely described by just three moments of the distribution. The purpose of this report is to summarize the progress after the first year of this LDRD program. We are confident that, had the program been allowed to follow its full 3-year course, significantly improved encapsulant materials would have resulted. It is noteworthy to point out that other laboratories are now actively carrying out similar work.

## Introduction

In practice, most polymers that are used in engineering applications are highly loaded with filler particles. These particles serve to control many critical physical properties including strength, modulus, thermal expansion, thermal conductivity, and density. Although materials scientists have studied filled polymer systems for many years, surprisingly little basic understanding exists regarding how the size, shape, distribution, surface chemical nature, and concentration of the filler particles affect the mechanical and rheological behavior of polymers during the curing process. Thanks to recent developments in computational modeling methods, and the revolution in raw computer power, it is now possible to gain an understanding of filled polymer systems that would have been impossible just a few years ago. The goal of this research is to apply state-of-the-art computational modeling methods to the important problem of filled polymers.

There are a number of important Defense Program (DP) applications of highly filled polymers of importance to Sandia. Most of the encapsulants used in packaging of electronic subsystems involve epoxies, silicones, and urethanes filled with particulates such as  $\text{Al}_2\text{O}_3$ , glass microballoons, and beta eucryptite. These fillers are used primarily to lower the thermal expansion coefficient of the polymer to closely match the glass and ceramic components and circuit boards in the electronic package. This is required in order to minimize thermal stresses that can ultimately lead to failure in the component. An important limiting factor that controls the amount of filler that can be introduced into the polymer is the resulting viscosity of the suspension; encapsulant processing is normally a "potting" process requiring a relatively low viscosity. Another crucial application of filled polymers is in elastomeric O-rings and seals. These systems involve crosslinked polymers of low glass transition that are normally filled with carbon black or silica particles to improve toughness. Indirect evidence suggests that the spatial distribution of the filler particles changes with time leading to changes in physical properties of O-rings in the stockpile.

Classical molecular modeling tools consist primarily of explicit 'exact' molecular simulation (Molecular Dynamics (MD) and Monte Carlo (MC) methods) and a number of approximate techniques ranging from crude mean field theory or perturbation theory (PT) to sophisticated integral equation and density functional theory. Each starts with defining a molecular entity and an intermolecular potential. Structural and thermodynamic properties are then obtained either via (time or ensemble) averaging (MD and MC respectively) or via (typically iterative) numerical solutions of (mostly integral) equations derived by approximate theories.

The composite material of interest here, filler particles in a polymer fluid, is particularly difficult. The primary reason is the disparity in size between the micron sized filler particles on the one hand and the molecular size of the polymers (100 nm) on the other. A brute force method involving an explicit MD simulation of both the polymer molecules and the filler particles is doomed because the small polymer molecules relax on a much shorter time scale than the large filler particles. As a consequence, small time steps are needed resulting in all the computing resources being spent moving only the polymer

chains while the filler particles are essentially stationary. In this approach, we overcome this fundamental limitation by combining two techniques: MD simulation and integral equation theory.

### Discussion and Results

The key step to bridging the disparate length scales is to transform the initial problem of filler particles in a polymer fluid into a system of filler particles only, in which the interparticle interactions depend on the polymer. Technically this is accomplished by integrating over all the configurations of the polymer fluid leading to the so-called solvation potential (sometimes referred to as the potential of mean force) which is the effective potential between two filler particles as mediated by the polymer. The smallest length scale has now been effectively eliminated from the modeling problem. This transformation is illustrated in Figure 1 below.

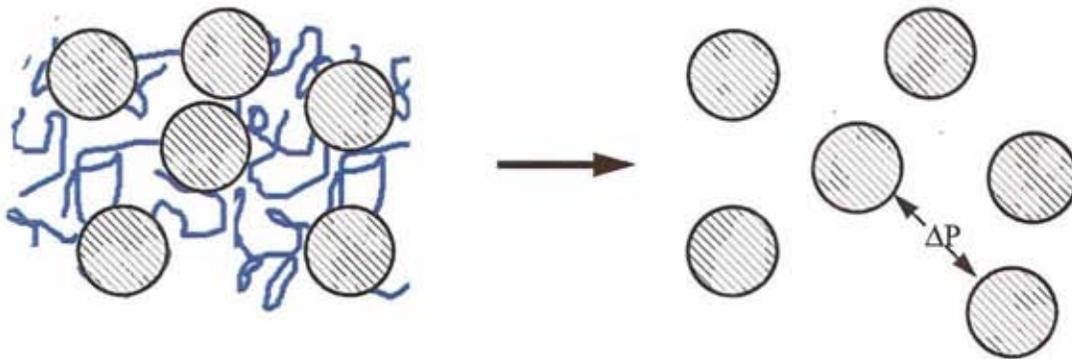
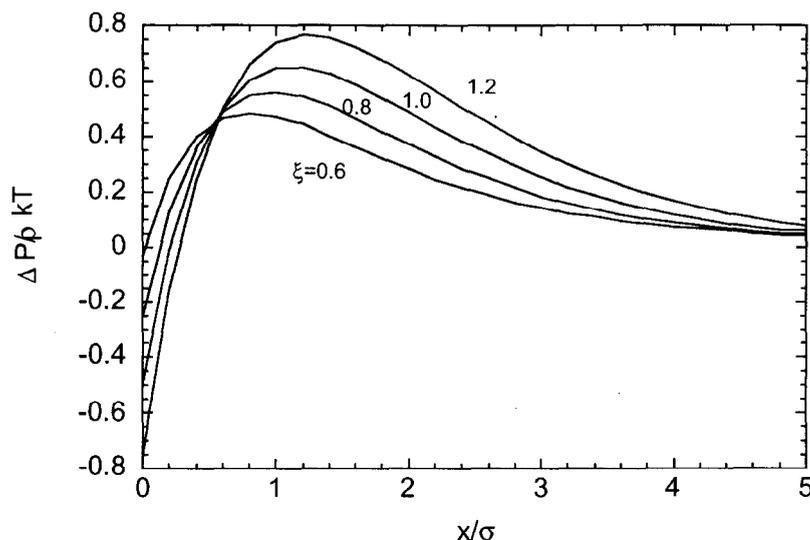


Figure 1 - Filler in a Polymer is Transformed into a System of Filler Particles with Effective Solvation Force,  $\Delta P$

The full problem consisting of both polymer and filler particles is shown schematically on the left. On the right, the degrees of freedom associated with the polymer molecules have been integrated out and replaced by an effective solvation force  $\Delta P$  that represents, in an average sense, the effect of the polymer matrix. The important thing to note is that this simplification is accomplished without disregarding the physics of the polymer — all the physics is contained in  $\Delta P$ , which now depends on temperature, polymer architecture, molecular weight, polymer density, as well as on the surface chemistry of the filler-polymer interface. In general, a number of routes are open to arrive at the medium-induced potential. We employed a polymer integral equation approach (PRISM) for a polymer sandwiched between two parallel flat surfaces to calculate the solvation potential. The effect of the curvature of the spheres is accounted for through the well-known Derjaguin approximation.

An example of a solvation force,  $\Delta P$ , computed from PRISM theory<sup>1</sup> for threadlike chains is shown in Figure 2.



**Figure 2** - Solvation Force for Threadlike Chains

This  $\Delta P$  has an interesting feature never seen in molecular systems, but familiar to colloidal suspensions of charged particles. The effective potential between spherical particles in Figure 2 is attractive at very short distances  $x$  between particles but repulsive at intermediate ranges of  $x$ . The shape of the solvation potential results from a subtle interplay between the range of the attractive interactions and a screening length  $\Delta P$  that depends on the radius of gyration and statistical segment length of the polymer, and the density. As in charged suspensions, this type of potential can be expected to explain stability versus flocculation. It is tempting to speculate that the short-range attractive nature of the solvation potential could lead to aggregation of filler particles in the composite. A powerful aspect of the solvation force approach is that it may also be possible to consider  $\Delta P(t)$  as a function of curing time. Thus, it may be feasible to mimic the effect of the polymers on the filler particles during the evolution of the crosslinking process.

Once the solvation potential is obtained, the smallest length scale now left in the problem is that of the filler particle. Similarly, the typical timescale is now set by the diffusion rate of the filler particles and no longer by the much smaller timescale of molecular vibrations of the polymer. This is an ideal situation as it allows one to rely on a battery of liquid-state physics techniques to predict the thermodynamic and structural properties of the filler-polymer composite. In addition it should be possible, through calculation of  $\Delta P(t)$ , to model how the physical properties evolve during curing.

In particular, for a given size distribution of filler particles, we used MC and/or MD to fully characterize the structure as a function of filler volume fraction, as expressed by radial distribution functions, Voronoi tessellation, and bond-order parameter distributions. These can be compared directly with structural information from experiments (cross sectional slicing, NMR, CTE, fluid viscosity). Similarly, we can calculate the thermal expansion coefficient. The most important dynamic quantity will be the viscosity that can be calculated from an MD simulation. This involves standard approaches based the stress-stress time correlation functions (equilibrium MD), or alternatively from a steady state shearing simulation (non-equilibrium MD, or NEMD). Having established a way to calculate the viscosity of a collection of filler particles interacting through a solvation potential, we are ready to tackle the trifold optimization problem that involves minimizing the thermal expansion coefficient while keeping the viscosity under a prescribed limit. The main variable is the particle size distribution.

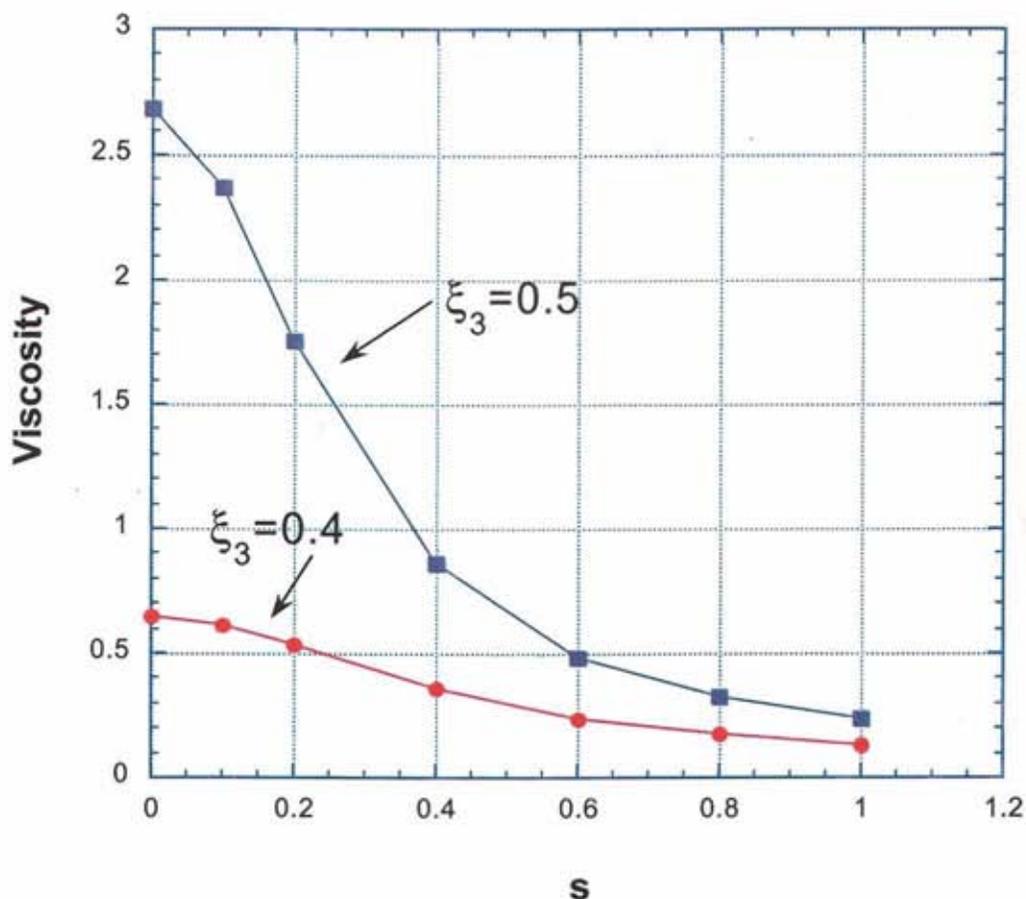
Generally speaking, optimizing for a size distribution can be a gargantuan task, as the distribution involves a very large number of parameters. For  $N$  particles, one can specify  $N$  sizes, and  $N-1$  mole fractions, or roughly  $2N$  total! To simplify the task we built on a recent advance of so-called three-moment hypothesis. This hypothesis states that the pressure of a hard sphere mixture is a function of just the first three moments of the sphere size distribution. The hypothesis is that hard sphere properties that depend on the volume fraction of spheres are to a good approximation also a function of just the first three moments. This hypothesis has been put to the test by investigating the maximum random packing fraction. It passes the test. It appears likely that a similar reduction of variables from too many (e.g.  $2N$ ) to just three is also possible for the viscosity.

### **Accomplishments**

A useful but tractable model of a filled polymer is to consider it a collection of spherical particles of varying sizes in a polymer. The goal is to optimize the distribution of particle sizes such that we maximize the packing fraction of filler while minimizing the viscosity. At first sight this is a daunting task, as optimizing a size distribution represents solving problem in a high-dimensional (or essentially infinite) parameter space consisting of size ratios and mole fractions. To solve the problem we decided to make use of some recent advances based on the statistical mechanics of liquid state theory.

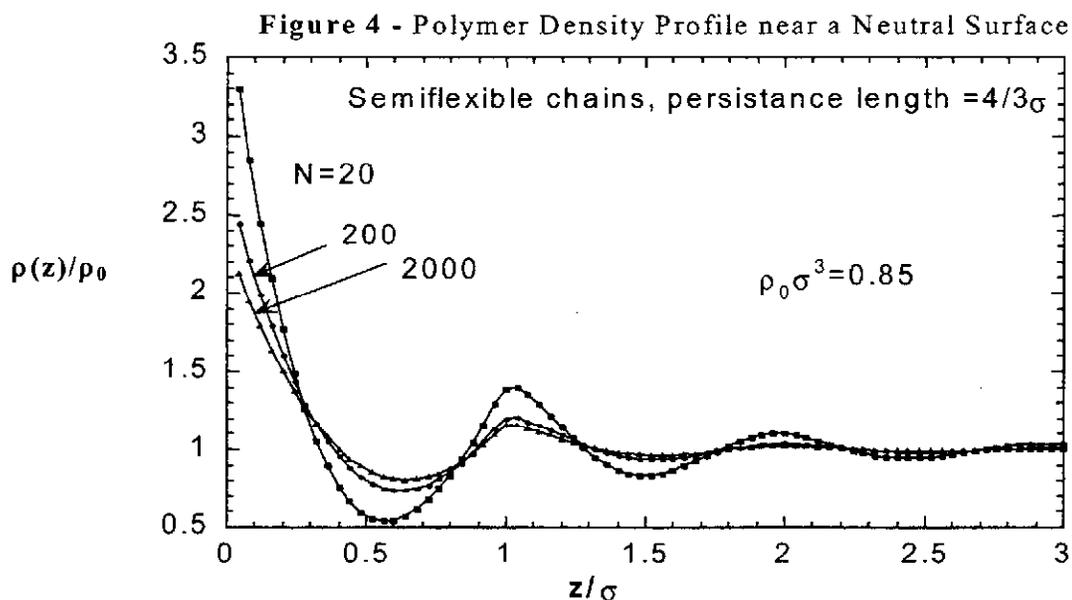
The “two-moment” approximation can be used to predict the viscosity of a hard sphere mixture once the viscosity of a monodisperse system is known. There are two ways to do this. In the first method, we make the *ansatz* that the viscosity is a function of the pressure and the two distribution moments. This allows the viscosity of a polydisperse mixture to be mapped onto that of an equivalent monodisperse system, namely that is at the same pressure as the polydisperse mixture. In the second method we hypothesize that the viscosity can be written as a function of the random closed-packed density,  $\Phi_{RCP}$ . (This is a description that has been tested in the colloidal literature). The latter is then considered a function of the two moments only. The two alternative methods do lead to different predictions for the viscosity as a function of the size distribution as shown in Figure 3.

**Figure 3 - Viscosity vs Standard**  
for a Polydispersed Hard Sphere Fluid



We have started to use simulation to test the underlying assumption that  $\Phi_{RCP}$  is a function of just two moments. This was initially done for symmetric distributions for which the second and third moments are linked and we are left with just a single distribution parameter. This simulation code for this problem has been adapted to run on a personal computer.

A key step in simplifying the problem of simulation of filler particles in a polymer matrix is to replace the effect of the polymer chains by an equivalent solvation potential acting between filler particles. This past year we studied the problem of semiflexible polymer chains between parallel surfaces. The distribution of polymer near the surfaces was calculated from Wall PRISM theory as a function of chain length  $N$  and chain stiffness,



characterized through a persistence length. Typical results are shown in the Figure 4 illustrating how molecular weight affects the polymer distribution in the immediate vicinity of the surface. In this figure, the distance between surfaces was 1 times the statistical segment length  $\sigma$  of the polymer. This information can be used to extract the solvation forces by studying how the wall profile varies with the spacing between the surfaces.

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