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14. ABSTRACT Solvent-free nanoparticle fluids, NFs, which were recently discovered in our group [1-10], offer exciting and unique opportunities for research and development for new materials technologies of potential interest to the Air Force. [1-10,11]. Specifically our focus is a new family of nanoparticle hybrids comprised of a charged corona grafted to inorganic nanoparticle cores. (Fig.1). These materials offer unique opportunities because their physical properties can be manipulated over a wide range by varying the size, shape, chemistry and concentration of the nanoparticles, type and length of the organic corona, and temperature. On one end of the spectrum are fluids characterized by optical and transport properties (conductivity and fluidity) remarkably similar to simple molecular liquids [13]. At the opposite extreme are systems which display properties similar to waxes and gels, and in some cases show evidence of solid-like ordering of the cores [3,6,7].						
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SUMMARY

The focus of this program was a new family of solvent-less nanoparticle fluids (hereafter referred to as nanoparticle fluids, NFs) comprised of a *charged* corona grafted to various nanoparticle cores. NFs possess flow properties (viscosity and diffusivity) remarkably similar to simple molecular liquids even in the absence of any diluent or solvent. Additionally, unlike molecular liquids, NFs do not possess a measurable vapor pressure dramatically increasing the range of potential applications. Furthermore, since NFs are hybrid systems, they can be engineered to combine specific properties (e.g. conductivity, magnetic susceptibility, refractive index, photoluminescence) that are difficult or impossible to achieve with molecular-based liquids.

These new materials offer new and unique opportunities because their physical properties can be manipulated over a wide range, from liquid to solid, by varying the size and concentration of the nanoparticles as well as the temperature. The fluid character at low temperatures especially in the absence of solvents facilitates many new applications where conventional colloidal suspensions either cannot be used or require special design to reduce solvent loss. Applications of potential interest to the Air-Force include lubricants for deployed space systems and MEMS, alternative coolants for thermal management applications, electrolytes for high-temperature fuel cells/batteries, ferrofluids for actuators, compliant electrodes, zero VOC inks for microfabrication, and high refractive index liquids.

Accomplishments – New Findings

Solvent-free nanoparticle fluids, NFs, which were recently discovered in our group [1-10], offer exciting and unique opportunities for research and development for new materials technologies of potential interest to the Air Force. [1-10,11]. Specifically our focus is a new family of nanoparticle hybrids comprised of a charged corona grafted to inorganic nanoparticle cores. (Fig.1). These materials offer unique opportunities because their physical properties can be manipulated over a wide range by varying the size, shape, chemistry and concentration of the nanoparticles, type and length of the organic corona, and temperature. On one end of the spectrum are fluids characterized by optical and transport properties (conductivity and fluidity) remarkably similar to simple molecular liquids [1-3]. At the opposite extreme are systems which display properties similar to waxes and gels, and in some cases show evidence of solid-like ordering of the cores [3,6,7].

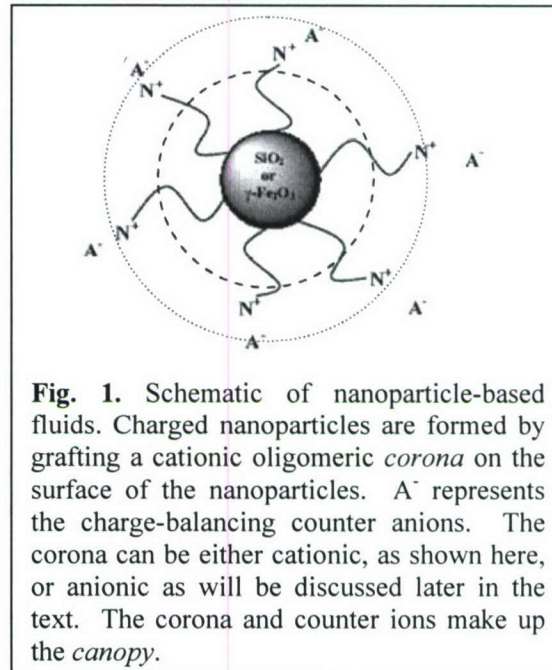


Fig. 1. Schematic of nanoparticle-based fluids. Charged nanoparticles are formed by grafting a cationic oligomeric *corona* on the surface of the nanoparticles. A^- represents the charge-balancing counter anions. The corona can be either cationic, as shown here, or anionic as will be discussed later in the text. The corona and counter ions make up the *canopy*.

The solvent-less nanoparticle fluids, NFs, are *distinguished* from conventional colloidal suspensions (including nanoparticle-based) in at least three ways. First, the tethered corona and associated counter ions are the “suspending medium” for the particles. This feature eliminates any need for an explicit solvent. Because the “solvent” is permanently attached, their effective vapor pressure can be rendered immeasurably small over a wide temperature range. The lack of solvent will facilitate many new applications (e.g. lubricants for deployed space systems and MEMS [11], alternative coolants for thermal management applications, electrolytes for high-temperature fuel cells/batteries, zero VOC inks for microfabrication, compliant electrodes, ferrofluids for actuators or high refractive index liquids), where conventional colloidal suspensions either cannot be used or require specialized design conditions to reduce solvent loss. Second, if interactions between the charged corona molecules favor spontaneous ordering in liquid-crystal or semi-crystalline arrays, it might be possible to spontaneously organize the attached nanoparticle cores into unusual motifs, yielding new materials with novel property profiles. Finally, because NFs are hybrids it is, in principle, possible to generate homogeneous liquids with essentially any core chemistry or shape. This opens up opportunities for fluids with a much wider range of physical properties (e.g. refractive index, thermal and electrical conductivity, magnetic susceptibility, photoluminescence) than typically possible with simple molecular liquids.

Our work has shown that even in the absence of solvent, nanoparticles can undergo reversible solid/liquid transition near or even below room temperature [1-10]. A solid-to-liquid transition is advantageous because it is accompanied by dramatic enhancements in transport properties, such as conductivity, diffusivity, and fluidity, which can be exploited in a variety of applications. A

fundamental requirement seems to be that thermal motion exerted by the corona on the nanoparticles must be large enough to overcome coagulation and settling.

The objective of this program is to provide a better understanding of the nature and strength of the interactions between the different constituents in the system and of how these interactions might affect phase behavior and transport properties such as conductivity, diffusivity, and fluidity (reciprocal viscosity). Our goal is to quantify how phase behavior and properties are affected by particle and canopy characteristics and to propose physical models that can be used to describe properties of the materials.

Research Progress

In a series of papers our group has shown broad applicability of this concept to a number of different cores including oxide nanoparticles (i.e. SiO_2 , TiO_2 , $\gamma\text{-Fe}_2\text{O}_3$, ZnO) [2,4,8], clusters (C_{60} , $\text{H}_3\text{PW}_{12}\text{O}_{40}$) [1] carbon nanotubes [9] and metals [10]. Since $\gamma\text{-Fe}_2\text{O}_3$ is magnetic, solvent-less ferrofluids are now possible. The ZnO fluids combine fluidity with high quantum yield photoluminescence. The C_{60} fluids are also attractive because of their potential high thermal conductivity while the cluster based fluids exhibit high ionic conductivity.

The NFs are typically synthesized by grafting a charged, oligomeric corona onto the nanoparticle cores. For example, reaction of $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{N}^+(\text{CH}_3)(\text{C}_{10}\text{H}_{21})_2\text{Cl}^-$ with hydroxyl groups present on the surface of oxide nanoparticles leads to a permanent, covalent attachment of a corona onto the nanoparticles and renders the nanoparticles cationic (Figure 1). Cl^- is initially present to balance the charge, in essence forming a nanoparticle salt. When chloride is the counter anion, the silica nanoparticles are in a solid form. No phase transitions are observed even after heating to 200°C . In contrast, replacement of the chloride by sulfonate anions such as $(\text{C}_{13}\text{H}_{27}(\text{OCH}_2\text{CH}_2)_7\text{O}(\text{CH}_2)_3\text{SO}_3^-)$ yields a *liquid* at room temperature. If the counter anion is isostearate, $(\text{CH}_3(\text{CH}_2)_{23}\text{CH}_2\text{COO}^-)$, a *gel-like* material is obtained.

To get a better understanding we have initiated a series of experiments designed to probe the structure and dynamics of a series of model nanoparticle fluids based on SiO_2 nanoparticles. Dielectric relaxation spectroscopy, Brillouin light scattering, shear rheometry, photoluminescent quenching and X-ray scattering have been used to provide some insight into the structure and dynamics of two model silica nanoparticle fluids and their behavior [6,7]. The first system is based on isostearate as the counter anion while the other on sulfonate (see above). In both systems hard silica nanoparticle cores are surrounded by the same corona of flexible, positively charged aliphatic chains. The positive charges reside on the ammonium group, which is separated from the silica core by a short carbon atom spacer. Strong Coulombic and ion-pair interactions dictate that the anions are in close proximity to the ammonium groups, which are covalently attached by the short spacer to the nanoparticle surface. Thus, the size and nature of the anion are expected to significantly affect packing and, therefore, the fluidity of the system. In addition, due to the hard-soft nature of the constituents as well as the presence of ionic and non-ionic domains, inhomogeneities at different length scales are expected to be present and to have a significant effect on the behavior of these materials.

Although the reasons for the fluidity are not yet completely understood, a working scenario is emerging [7]. According to this scenario the bulky and highly asymmetric ions lead to frustrated molecular packing in the system and much weaker interactions than in the Cl^- analog. Using

differential scanning calorimetry and dielectric spectroscopy we find that the glass transition temperature of the sulfonate and isostearate systems and, hence, the local dynamics are surprisingly similar suggesting weak anion association in both systems. However,

despite the very similar local mobility, the two systems exhibit very different flow properties. Figure 2 shows the master curve of the storage G' and loss G'' shear modulus for both systems as a function of

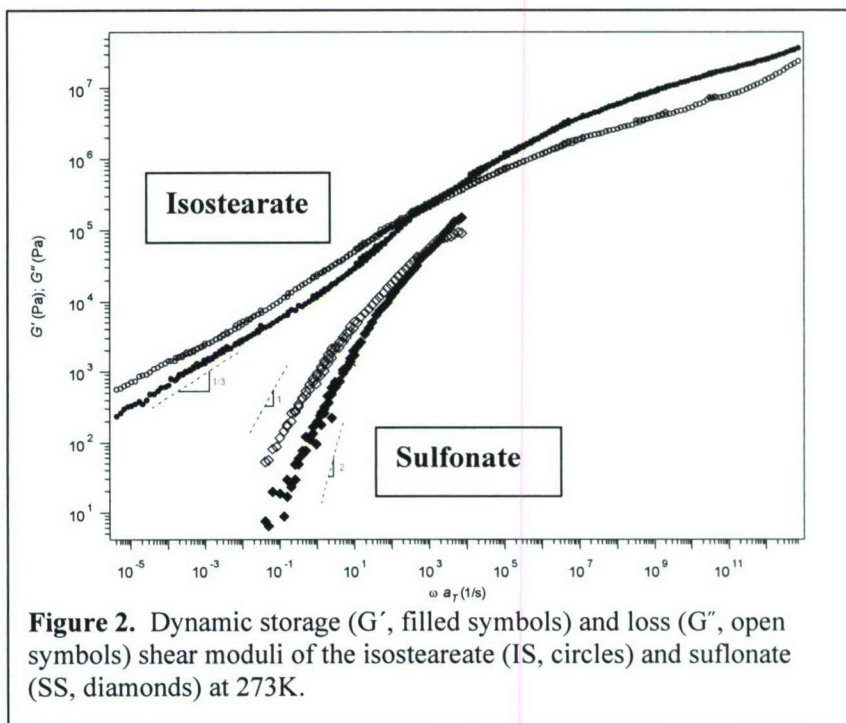


Figure 2. Dynamic storage (G' , filled symbols) and loss (G'' , open symbols) shear moduli of the isostearate (IS, circles) and sulfonate (SS, diamonds) at 273K.

reduced frequency, $a_T\omega$, at a fixed reference temperature of 273 K. Frequency reduction is achieved using the time-temperature superposition principle. G' and G'' for both systems intersect at nearly identical frequencies ($\tau \approx 1$ ms at 273K) suggesting that the same relaxation process is responsible for energy dissipation. At frequencies below the crossover point, however, the sulfonate based NF shows a quick transition to a near terminal scaling behavior (i.e. $G'' \sim \omega > G' \sim \omega^2$) characteristic of dissipation-dominated or liquid state. In contrast, the isostearate system exhibits a more complex behavior. While G'' is higher than G' , indicating that the material more effectively dissipates than stores mechanical energy on times scale greater than 1 ms, the frequency dependence of modulus ($G'' > G' \sim \omega^{1/3}$) is intermediate between a disordered solid and a simple liquid. The more complex, gel-like flow behavior seen in the isostearate system relates to a liquid-like ordering observed by Small Angle X-ray Scattering. This enhanced structuring was also manifested as a second slow dynamic process in the dielectric loss spectrum.

More recently we have demonstrated a new, complementary approach for synthesizing NFs. The new approach is scalable and can produce large quantities of material. The first step involves surface functionalization of the particles by condensation of 3-(trihydroxysilyl)-1-propane sulfonic acid (SIT) with surface silanol groups as shown in Fig. 3. This charged organosilane renders the nanoparticles anionic, where a proton is present to provide charge neutrality to the system. In this form, the nanoparticles are white powders in the absence of solvents and show no visible phase transitions when heated up 200 °C. As Fig. 3 shows, NFs are then produced by the reaction of a strong acid in the form of the sulfonate functionalized silica nanoparticles with a tertiary amine ($C_{18}H_{37}N[(CH_2CH_2O)_mH][(CH_2CH_2O)_nH]$) which serves as a weak base. This reaction produces amber-colored materials whose fluidity can be varied simply by controlling the

volume fraction of cores. The TEM image in the inset of Figure 3 shows non-aggregated particles consistent with the optical transparency of the samples.

Since the final synthetic step in NFs involves the reaction of a strong acid with a weak base, the true equivalence point should occur at a pH below 7. In **Fig. 4**, a plot of the reaction pH as a function of the added amine concentration is shown. From the plot it is clear that the equivalence point for this particular set of functionalized nanoparticles occurs at a pH ~ 4 , corresponding to a silica content of 42 wt. %. **Fig. 2**, therefore, serves as a phase diagram showing the transition from a suspension of NFs into excess amine to amine starved NFs, with the transition occurring at a core concentration corresponding to the equivalence point of the reaction.

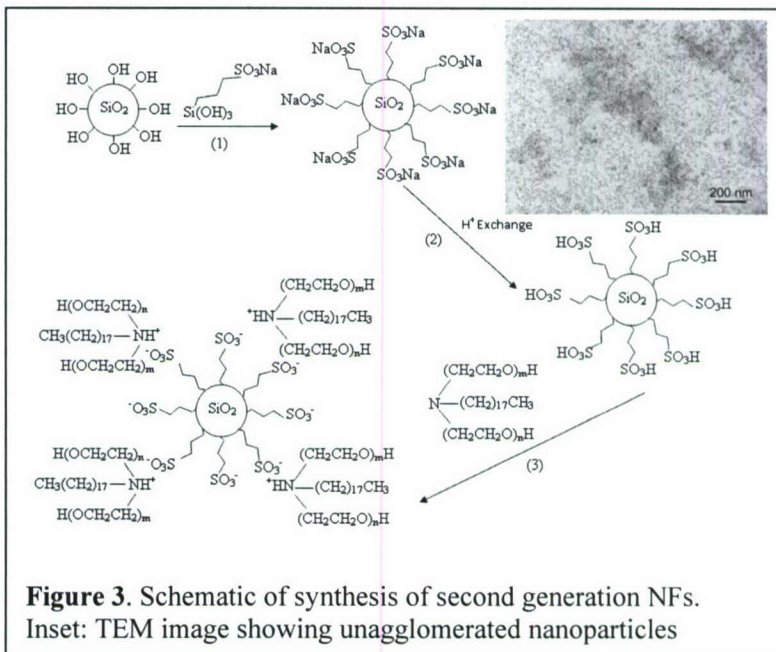


Figure 3. Schematic of synthesis of second generation NFs. Inset: TEM image showing unagglomerated nanoparticles

For this particular system stoichiometric NFs correspond to SiO_2 core concentration of 42 wt.%. When an excess of the amine is present, it serves as a plasticizer increasing the fluidity of the system. On the other end of the spectrum are materials with high nanoparticle core content, which display properties similar to waxes, gels, and crystalline solids.

The overall behavior of NFs is determined not only by the properties of the tethered organosilane and associated counter-ions, but also by the concentration of nanoparticle cores present. **Fig. 5** illustrates the effect of core concentration on the viscoelastic properties of NFs at 28 $^\circ\text{C}$. At a SiO_2 concentration of 19 wt. %, Newtonian liquid behavior is observed as evidenced by the frequency independent complex viscosity, $\eta^*(\omega)$ (lines). For higher SiO_2 concentrations, complex viscoelastic behavior is

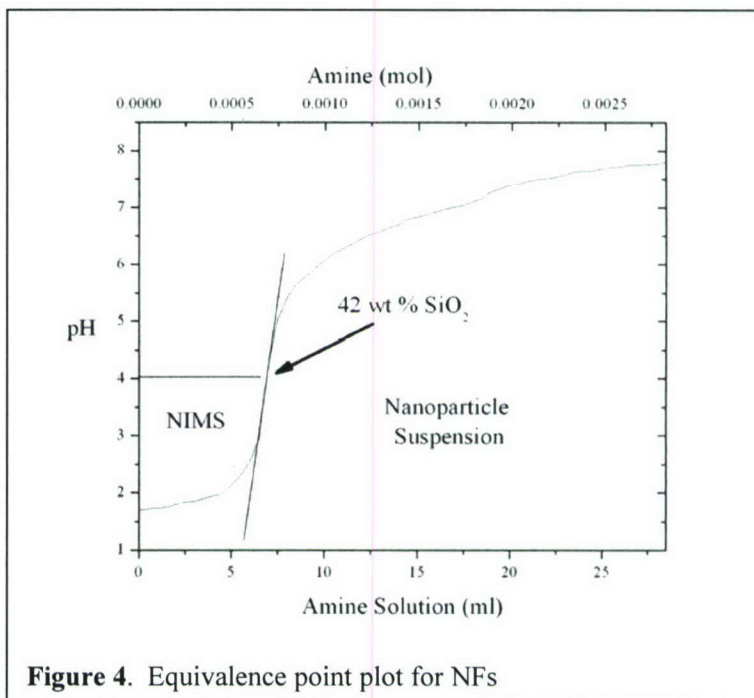


Figure 4. Equivalence point plot for NFs

observed through the frequency-dependent moduli and complex viscosity. In addition, steady-state shear rheometry reveals details about the interparticle interactions and Brownian motion of the cores. **Fig. 6** shows a plot of the viscosity as a function of shear stress for NFs with a nanoparticle core content of 26wt%.

Fig. 6 illustrates that the post yield flow properties of NFs cover the full spectrum of complex fluid behavior; from simple Newtonian shear viscosity at low shear stresses, to non-Newtonian shear-thinning at intermediate stresses, and shear thickening at high stresses. Steady-state shear measurements indicate that even dense NFs (35 wt. %) show a solid-like yield at low shear stresses, $\tau_y \approx 0.25$ Pa, which is $\sim 1/1000$ of the elastic modulus G_{eq} , to produce a Newtonian liquid at low shear rates. It is also possible to estimate a characteristic structural relaxation time from the reciprocal of the shear rate at which the steady-state shear viscosity becomes shear-rate dependent (inset, Fig 4a). Measurements show that NFs with a core concentration of 35 wt. % have a characteristic relaxation time $\lambda_s \approx 4.1 \times 10^5$ s which is much too large to result from a molecular process involving the organosilane and amine counter-ion species. This is most likely the timescale for Brownian motion of the surface functionalized cores in the medium composed of the organosilane and amine species. Measurements of NFs with a 19 wt. % core concentration reveal characteristic relaxation times of about 5.0×10^{-2} s.

The relative viscosity of NFs follows the same behavior as that observed in conventional colloidal suspensions, where the relative viscosity increases with increasing volume fraction (ϕ) until eventually diverging at a critical volume fraction associated with the glass transition. Not only do these systems show similar behavior, but standard models such as the Krieger-Dougherty equation and the Thomas equation fit the data reasonably well.

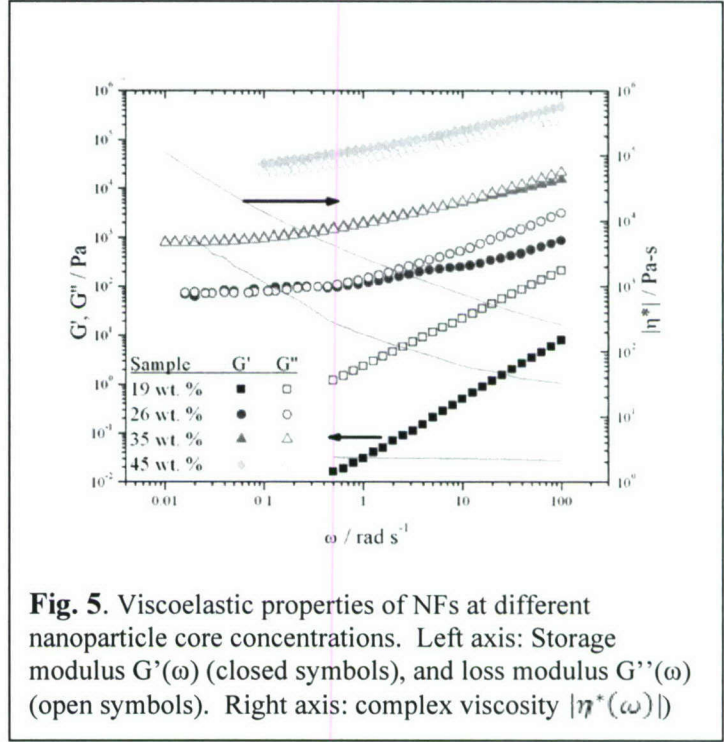


Fig. 5. Viscoelastic properties of NFs at different nanoparticle core concentrations. Left axis: Storage modulus $G'(\omega)$ (closed symbols), and loss modulus $G''(\omega)$ (open symbols). Right axis: complex viscosity $|\eta^*(\omega)|$

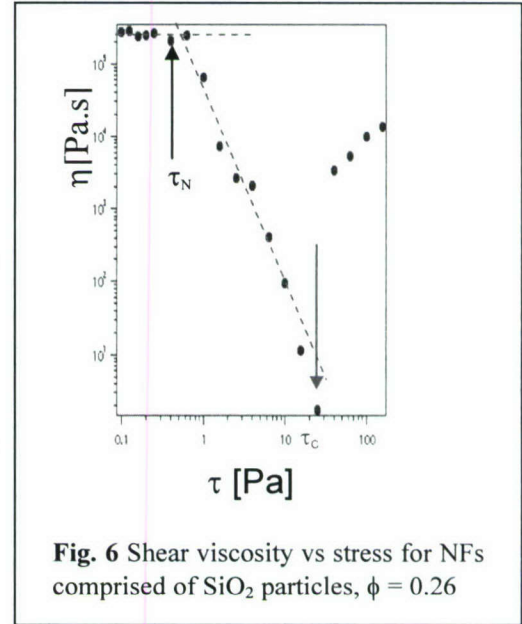
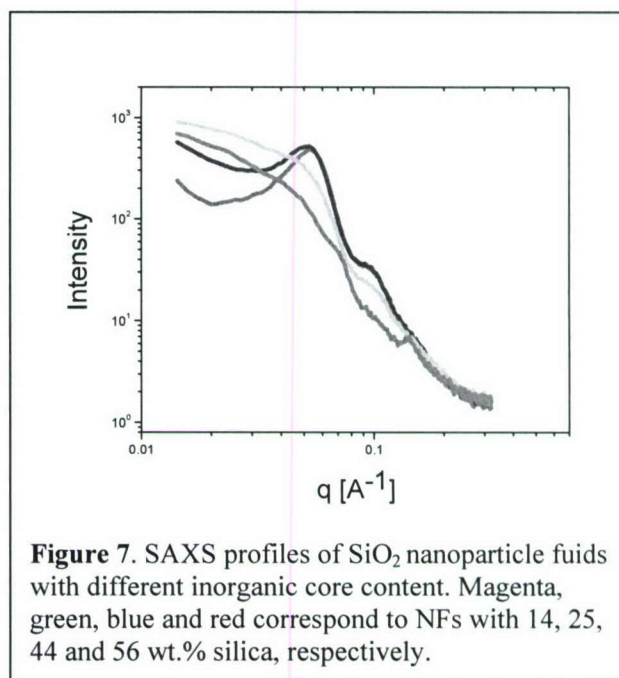


Fig. 6 Shear viscosity vs stress for NFs comprised of SiO_2 particles, $\phi = 0.26$

Preliminary structural studies using wide-angle and small-angle X-ray diffraction (WAXS and SAXS) provide information about local packing, spatial coherence, and long range order. When there are no interparticle correlations (i.e. low concentration of nanoparticle cores) the scattering profile will be modeled in terms of a dilute suspension of scatterers. As the concentration of nanoparticle cores increases, scattering profiles characteristic of interacting nanoparticles start emerging and can be modeled accordingly (Figure 7).



Personnel Supported

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Interactions/Transitions

We are collaborating with Kodak, Summit Lubricants and IBM and Rohm and Haas (with a contract from Sematech) to evaluate NFs in various applications as inks, lubricants and high refractive index media for immersion lithography, respectively.

New discoveries, inventions, or patent disclosures

A.B. Bourlinos and E.P. Giannelis, "Functionalized Nanostructures with Liquid-like Behavior", US2007/0254994 A1.

Honors/Awards

None