

# Exceptional properties of semi-dilute solutions of nanoparticle laden polymers in water

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Dr. Wang will lead studies of the structure of nanoparticle laden polymeric solutions using small angle X-ray scattering at the Advanced Photon Laboratory of the Argonne National Laboratory. The other parts of this study will be led by Prof. Joseph in collaboration with Prof. Satish Kumar of the Department of Chemical Engineering at the University of Minnesota.

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### ABSTRACT

This proposal is motivated by three recently discovered properties of semi-dilute aqueous solutions of composite polymers of polyethylene oxide and silica nanoparticles (in the size range from 10 to 100 nanometers). We believe that a composite macromolecule with exceptional properties is created by the absorption of the polyethylene oxide onto the silica nanoparticles.

(1) The solutions with nanoparticles exhibit exceptional properties in extensional flow giving rise to dramatic increases in the pulling power of tubeless and open siphons.

(2) The nanosolutions are unusually effective in cleaning surfaces; under high rates of extension the solution is stiffened and then can be pulled off a substrate like an adhesive tape. Just which and why some surfaces are so effectively cleaned is not understood.

(3) The nanoparticle / polymer solutions show a marked resistance to oxidation; their rheological behavior is stable over time compared to the very marked degradation of these properties in the polymer solutions without nanoparticles. Polyethylene oxide can be stabilized by silica nanoparticles and Polyacrilamide may also be stabilized. This stabilization has potential for commercial and technological application. The degradation of polymer solutions, for example, severely restricts their applications to technologies like drag reduction.

The mechanism by which the seeding of nanoparticles prevents the degrading of polymer solutions is not understood. One idea is that the nanoparticles absorb precisely on the sites on which the oxidation is greatest; the nanoparticles then are a blocker analogous to proteus inhibitors of viruses.

The goal of this research is to understand the exceptional properties of macromolecule solutions of polymers seeded with nanoparticles in water. However, recent experiments of Wang & Joseph 2003 [20] haven shown that the addition of inert, neutrally buoyant submillimeter particles in modest concentrations (<10% by volume) induce exceptional siphoning properties similar to those seen in the "nanosiphons". These inert particles are not nanoparticles and they do not chemically bond to PEO.

Evidently the explanation of the performance of the particle laden tubeless siphon is to be found in the analysis of flow induced particle-fluid forces and not in molecular structure. In these solutions, we believe that the enhancements are due not to a chemical bridging (adsorption of PEO on the particles), but rather to a mechanical bridging in which a stress field is set up that highly couples the motion of different macromolecules. It is hard to believe that the similarity between nanosiphons and particle-laden tubeless siphons is fortuitous, but it is a mystery and it ought to be studied.

## I. Prior literature

The only prior literature on particle laden tubeless siphons (Wang & Joseph 2003) and nano particle laden tubeless and open siphons (Wang, Bai & Joseph 2003) is in the two papers summarized in the following abstracts:

J. Wang & D. D. Joseph 2003. Particle-laden tubeless siphon. *J. Fluid Mech.* **480**, 119-128.

A tubeless siphon was created by sucking a 1% aqueous Polyox<sup>†</sup> solution laden with particles from a beaker into a cylinder by a moving piston. The piston speed and particle concentration were varied. At very high rates of withdrawal, all the liquid could be removed before the siphon broke. In this case, the beaker was completely cleaned without a trace of liquid. The addition of small concentrations of small, nearly neutrally buoyant particles greatly enhanced the pulling power of the liquid, reducing the threshold speed of withdrawal at which the beaker was completely cleaned. At speeds of withdrawal smaller than the threshold not all of the fluid-particle mixture is pulled out of the beaker. The amount pulled out first increases, then decreases as the particle concentration is increased.

J. Wang, R. Bai & D. D. Joseph 2004. Nano-particle laden tubeless and open siphons. *J. Fluid Mech.* **516**, 335-348.

Tubeless and open siphons are unusual types of siphons which operate without conduits, in the open, supported only by extensional stresses. Here, we demonstrate that the addition of silica nanoparticles in modest concentrations (of the order of 1% by weight) to a moderately dilute aqueous Poly(ethylene oxide) (PEO) solution of a moderately low concentration (0.5% by weight) has a dramatic affect on the power of the siphon as well as on the ability of the siphon to completely clean substrates. These enhanced effects may have a partly fluid mechanical explanation, since they also occur when the siphon is laden with inert sub-millimeter particles (Wang & Joseph, *J. Fluid Mech.*, vol. **480**, 2003, p. 119). The extensional properties of PEO solutions are greatly enhanced when they are loaded with silica nanoparticles. The degradation of the PEO solution is suppressed by the addition of silica nanoparticles.

There is no literature other than that in Wang *et al.* 2004 on the properties of semi-dilute solution of polymers seeded with nanoparticles in water. However, there is a relevant related literature about these macromolecular composites not in solution.

The available evidence suggests that the PEO molecules absorb onto the silica nanoparticles to form a composite macromolecule with unusual as yet to be understood properties. It is well known that the affinity between PEO molecules and silica particles is high, and the adsorption of PEO onto silica has been extensively studied (Howard and McConnell 1967; Killmann et al. 1985, 1988, 1994; Zaman et al. 2000). It is believed that the adsorption mechanism between PEO molecules and silica particles is through hydrogen bonding between the ether oxygen of PEO molecules and isolated silanol groups on the silica surface (the silanol group density on silica particles is  $\sim 4-5$  SiOH/nm<sup>2</sup>) (Rubio and Kitchener 1976).

We have not found a literature on nanoparticle enhancement of extensional stresses in polymer solutions. Zaman *et al.* (1996, 2000) treated the effects of absorbed PEO on the rheology of colloidal silica suspensions of much larger (of the order of 1  $\mu$ m) particles in much larger concentrations (up to 60% by volume). Their rheological studies focused on the shear viscosity of the PEO/silica suspension. Liu *et al.* (1994) studied the rheological behavior of nanometric silica beads in relation to the adsorbed amount of high molecular weight PEO. They observed different rheological behavior such as shear induced gelation, Newtonian, and thixotropic shear thinning depending on the adsorption level, number of particles per macromolecular chain, and free polymer equilibrium concentration.

The mechanism of nanoparticles bridged by polymer molecules has been studied extensively by Otsubo and co-workers. Studies of the shear viscosity and stress relaxation behavior of silica nanoparticle

suspensions in polyacrylamide (PAAm) solutions indicated elastic behavior at low frequencies when both the particle and polymer concentration is increased beyond certain critical levels (Otsubo & Watanabe 1987, Otsubo 1990, Otsubo & Nakane 1991). Flocculation of silica particles by polymer bridging was proposed to explain the observations and the boundary of the elastic behavior was investigated using percolation theory (Otsubo 1990, Otsubo & Nakane 1991). Shear viscosity behavior, normal stress and dynamic viscoelasticity were measured for copolymer nanoparticle suspensions flocculated by polymer bridging (Otsubo 1992, 1993, 1994a). It is believed that the polymer coil whose size is comparable in solution to particle diameter makes a flexible bridge between two particles. The reversibility of the bridge between the nanoparticle and polymer molecules was discussed based on the affinity between them (Otsubo 1994b, 1995, 1998, 1999). The polymer chains having strong affinity form fragile bridges between particles as a result of irreversible adsorption. The decrease in the adsorption affinity by the addition of small amounts of surfactant causes the reversible adsorption.

Zhang and Archer (2002) studied linear viscoelastic properties of PEO/silica nanocomposites. They measured the elastic and loss modulus of the nanocomposite melts and found a transition to a solidlike response at low oscillation frequencies for particle volume fraction  $\phi$  as low as 2%, which is dramatically lower than the theoretical percolation threshold ( $\phi \sim 30\%$ ) for solidlike behavior in conventional particle-filled polymers. To explain their observations, they suggested a filler networking mechanism, wherein nanosized silica particles surrounded by an immobilized shell of PEO are bridged by much larger polymer molecules.

The tubeless and open siphon of nanoparticle suspensions reported here is related to the extensional property of the suspension and has not been studied before. The filler networking mechanism with particles bridged by polymer molecules may explain the dramatic enhancement of the siphons. This mechanism provides strong cohesive forces to support the siphon column, enabling the siphon to pull out more liquid. We propose to investigate this mechanism by characterizing the structure and rheology of the nanoparticle-laden polymer solutions and correlating the resulting information with the flow properties we observe.

## II.1 Tubeless and open siphons

The tubeless siphon (figure 1) is one of the wonders of the dynamics of polymeric liquids; it is not observed in Newtonian fluids. Pictures of the tubeless siphon appear in nearly all of the recent books on the subject, but the siphon is not understood. Bird *et al.* (1977) remark that "... it is believed that it is the orientation and elongation of polymer molecules along the streamline that are responsible for the large axial stresses that make the siphon work." Despite the prominence given to tubeless siphons as an example of non-Newtonian behavior, coherent explanations of the mechanical and rheological fundamentals which make the siphon work are lacking.

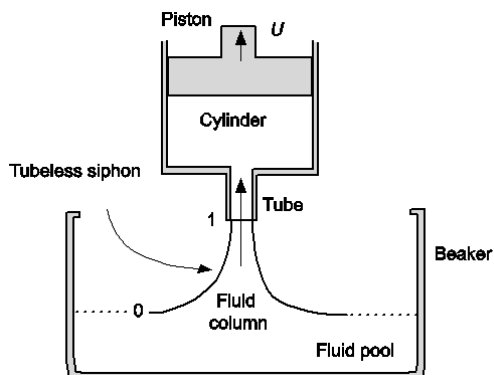


Figure 1. Tubeless siphon: a fluid is sucked through a nozzle elevated above the surface of the fluid. Instead of the fluid breaking as for a Newtonian fluid, an unsupported fluid column is drawn from the pool below into the nozzle without breaking.

Ordinary siphons usually break because air enters the siphon tube. If the lowest pressure in the system at the top of the siphon falls below the vapor pressure, the siphon will break; usually air enters before cavitation occurs. The action of the open siphon (figure 2) depends upon the influence of gravity and upon the cohesive forces of polymeric liquids which prevent the siphon column from breaking. The difference between the tubeless siphon and the open siphon is analogous to the difference in vertical tubes of motions driven by pressure gradients and motions driven by body forces.

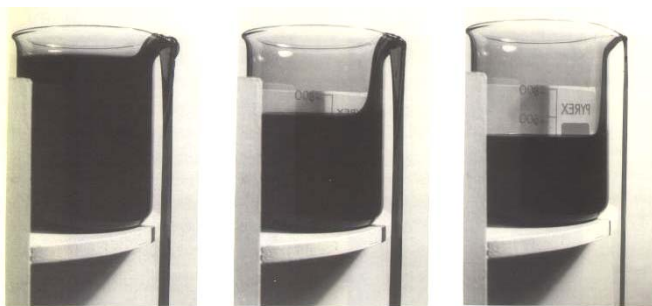


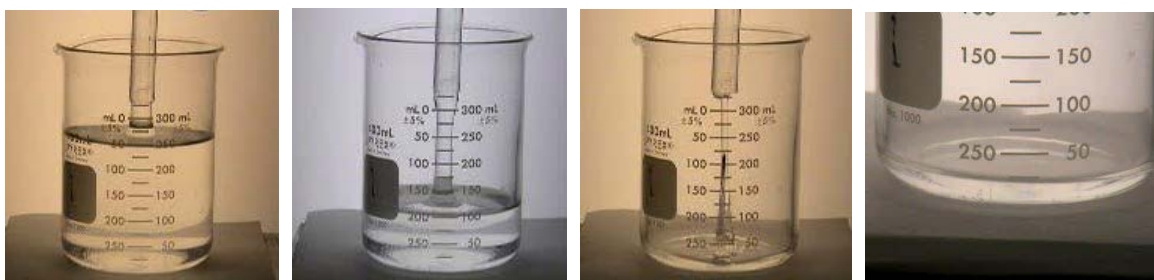
Figure 2. The open-siphon effect of a 0.75% aqueous solution of PEO. Only the slightest spilling will part empty the beaker. (Boger & Walters 1993).

## II.2 Nanoparticle laden tubeless and open siphon

Experiments which demonstrate the increases in siphoning power and cleanup which may be achieved by seeding PEO with silica nanoparticles were reported by us in Wang *et al.* 2004.

### Tubeless siphon

The experimental setup for the tubeless siphon is shown in figure 1. We compare the tubeless siphon of a 0.5 wt% 4 million g/mol PEO solution with and without nanoparticles in figure 3; the other conditions such as the initial volume and the piston speed  $U$  are the same in the two cases. Without nanoparticles, there is a puddle of liquid left in the beaker after the siphon (figure 3(a)); with 2.34 wt% silica nanoparticles, the siphon has a much thicker fluid column and lasts longer time and a complete cleaning is achieved (figure 3(b)). The movies of the tubeless siphon experiments are available at <http://www.aem.umn.edu/people/faculty/joseph/particles/nano/index1.html>

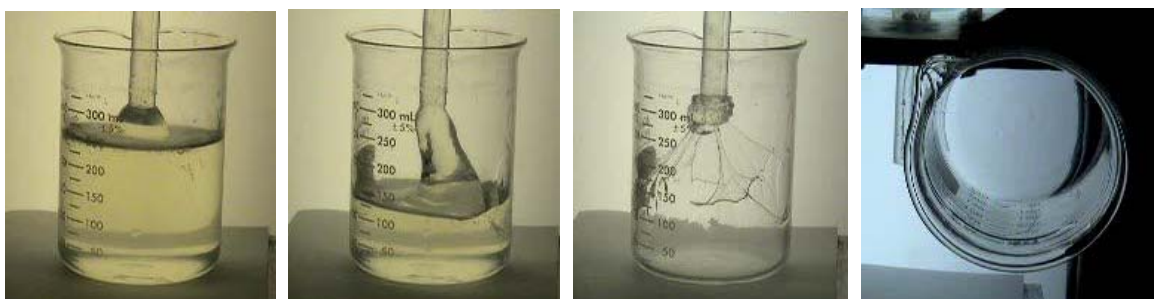


(a) Elapsed time: 8 sec

16 sec

21 sec

23 sec



(b) Elapsed time: 8 sec

16 sec

27 sec

28 sec

Figure 3. Tubeless siphon of a 0.5 wt% 4 million g/mol PEO solution with and without nanoparticles; the initial volume and the piston speed are the same in the two cases. (a) Without particles, about 20-ml liquid is left in the beaker after the siphon. (b) The PEO solution is laden with 2.34 wt % 10 –20 nm silica particles. The tubeless siphon is much stronger and a complete cleaning is achieved.

An emptying fraction  $F$  can be defined as the ratio of the volume emptied from the beaker to the initial volume of the suspension. We show  $F$  as a function of the piston speed  $U$  using different

PEO/silica suspensions in table 1. The addition of only 1.18 % by weight silica nanoparticles can improve the emptying fraction  $F$  from 35% to almost 100% at a low piston speed ( $U = 0.070$  cm/s). At higher silica nanoparticle concentrations, the suspension can be completely cleaned up, leaving a virtually dry beaker. Significant swelling in the liquid column was observed during the siphon indicating strong normal stresses. In the range of the concentrations we studied (up to 4.74% by weight), the pulling power of the suspension increases with the nanoparticle concentration.

PEO (wt %)	Silica (wt %)	$U$ (cm/s)	$F$
0.5	0	0.070	35%
		0.128	82%
		0.185	88%
		0.243	93%
0.5	1.18	0.070	99%
		0.128	100%
		0.185	100%
		0.243	100%
0.5	2.34	0.070	100%
0.5	4.74	0.070	100%

Table 1. The emptying fraction  $F$  as a function of the piston speed  $U$  using different PEO/silica suspensions. The molecular weight of the PEO is 4 million g/mol and the size of the silica particles is 10–20 nm in these samples.

### Open siphons

In the open siphon experiment, the beaker holding the testing fluid is tilted for an angle  $\alpha$  so that a portion of the fluid spills out of the beaker. If the fluid is Newtonian, the flow stops when the fluid surface levels with the edge. For viscoelastic fluids, the flow can continue to empty the beaker partially or even completely (see figures 4 and 5 where the fluids are PEO/silica suspensions). The movies of the open siphon experiments can be viewed at

<http://www.aem.umn.edu/people/faculty/joseph/particles/opensiphon/>.

The strength of the open siphon is affected by the tilting angle  $\alpha$ . For Newtonian fluid, the flow stops when the fluid surface levels with the edge. If we assume that before the siphon the beaker is full of fluid, then a simple geometric derivation would show

$$V_L = V_0 - \pi a^3 \tan(\alpha) \quad (1)$$

where  $V_L$  is the volume of the fluid left in the beaker after the siphon,  $V_0$  is the original volume of the fluid, and  $a$  is the radius of the beaker (suppose the beaker is approximated by a cylinder). Obviously the volume left in the beaker would decrease as the tilting angle increases.

We carried out open siphon experiments with tilting angles from 10° to 50° using 0.5 wt% aqueous PEO solutions laden with silica nanoparticles. In all the experiments, the original volume  $V_0$  is 271 ml. The volume left  $V_L$  is plotted against the tilting angle  $\alpha$  in figure 6. The experimental data using water is also plotted. Figure 6 shows that as  $\alpha$  increases,  $V_L$  decreases faster for PEO/silica suspensions than for water.

We measure the properties of different PEO/silica suspensions in open siphon experiments with the tilting angle fixed at 15° and the initial height of the siphon column  $h_i$  fixed at 42.3 cm. In all the experiments, the beaker is full of fluid before the siphon,  $V_0 = 271$  ml. Let  $V_1$  stand for the volume of a Newtonian fluid left in the beaker after the flow stops.  $V_1 = 240$  ml in our case. We define the emptying fraction  $F$  as

$$F = \frac{V_1 - V_L}{V_1} \times 100\% . \quad (2)$$

The reason we use  $V_1$  instead of  $V_0$  to define  $F$  is that the portion of the fluid ( $V_0 - V_1$ ) flows out of the beaker simply due to gravity and should not be used to characterize the viscoelasticity of the testing fluid. Under the definition (2),  $F = 0$  for a Newtonian fluid and  $F = 100\%$  when a complete cleaning is achieved. In figures 4 and 5, we show snapshots of the open siphon experiments using different PEO/silica suspensions. The measured values of the emptying fraction are listed in table 2 and plotted in figure 7.

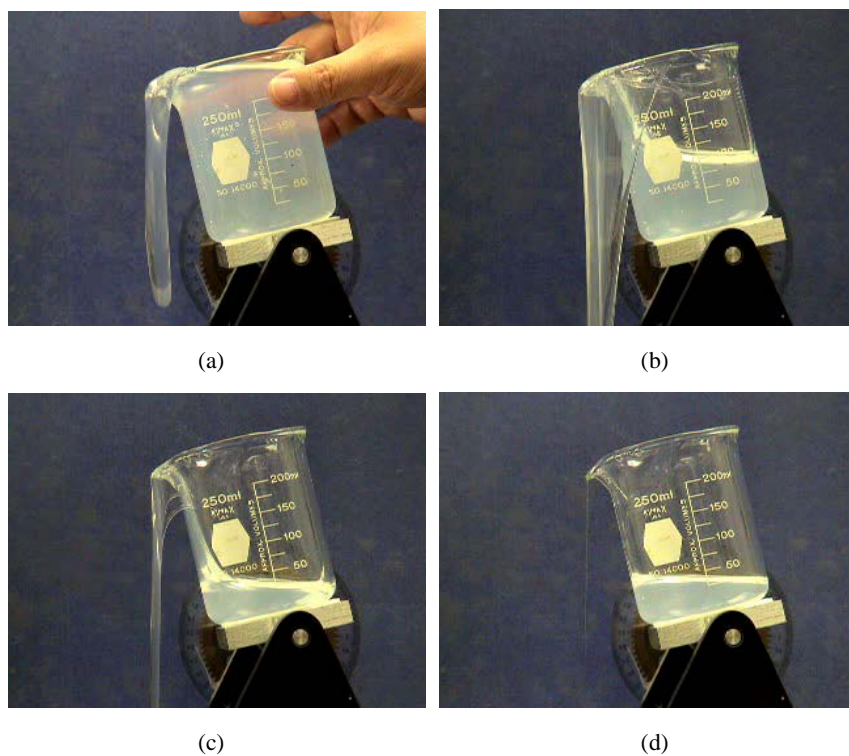


Figure 4. Photos of the open siphon experiment using a 0.5 wt% 8 million g/mol PEO solution laden with 2 wt% 10 – 20 nm silica particles. Elapsed time: (a) 2.4 s; (b) 4.6 s; (c) 22.5 s; (d) 60 s. About 30 ml fluid is left in the beaker after the siphon. [Click here to see the movie.](#)

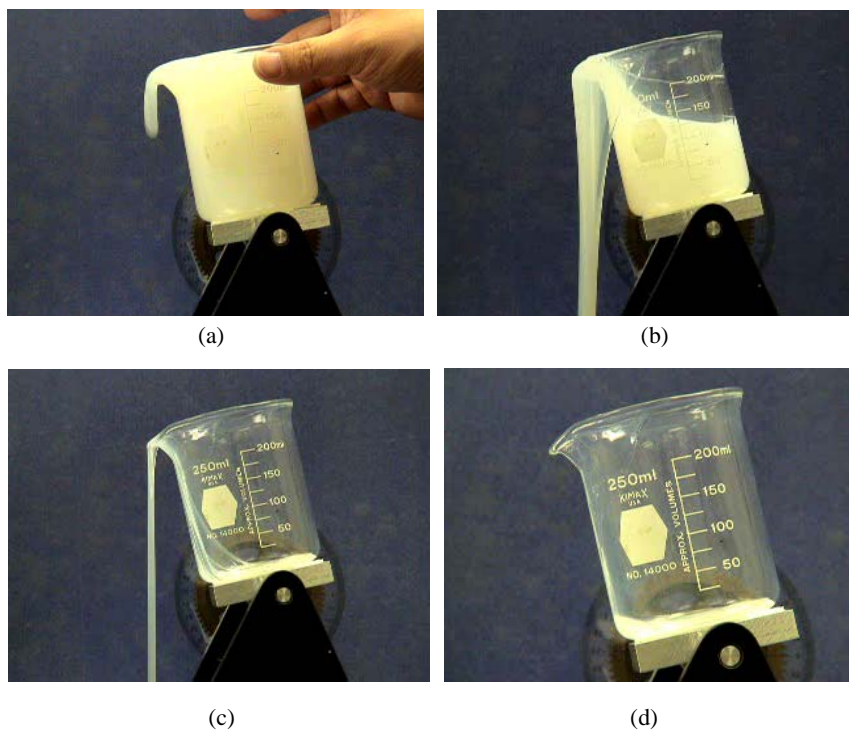


Figure 5. Photos of the open siphon experiment using a 0.5 wt% 8 million g/mol PEO solution laden with 2 wt% 45 – 60 nm silica particles. The suspension is almost cleaned up by the siphon. Elapsed time: (a) 1.5 s; (b) 3.0 s; (c) 6.0 s; (d) 14.5 s. [Click here to see the movie.](#)

PEO MW (g/mol)	PEO (wt %)	Silica (wt %)	Silica size (nm)	$F$
8 million	0.5	0	-	77.1%
		0.5	10 – 20	20.8%
		1.0		62.5%
		2.0		87.5%
		0.5	45 – 60	92.5%
		1.0		98.3%
		2.0		99.1%
4 million	0.5	0	-	50.5%
		0.25	45 - 60	58.3%
		0.5		70.6%
		0.75		81.5%
		1.0		89.1%
		1.25		89.5%

Table 2. Measurements of the emptying fraction  $F$  in the open siphon experiments of different PEO/silica suspensions. The tilting angle in these experiments is  $15^\circ$  and the initial height of the siphon column  $h_1$  is 42.3 cm.

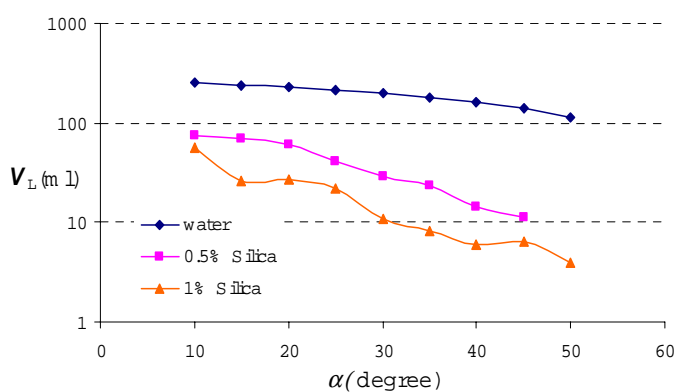


Figure 6. The volume  $V_L$  left in the beaker after open siphon as a function of the tilting angle  $\alpha$ . The three curves are for water, PEO solutions laden with 0.5 wt% and 1 wt% 45 – 60 nm silica particles. The molecular weight of PEO is 4 million g/mol and the concentration of PEO in the solutions is 0.5 wt%.

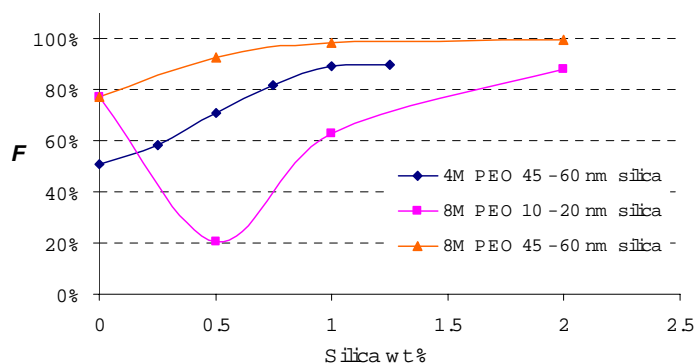


Figure 7. Effects of the silica nanoparticle concentration in PEO solutions on the emptying fraction  $F$ . The data is from table 2.

The data in table 2 and figure 7 shows that the addition of 45 – 60 nm silica particles to PEO solution (4 million or 8 million g/mol) increases the emptying fraction  $F$  monotonically; the addition of 10 – 20 nm silica particles to 8 million g/mol PEO solutions first decreases  $F$  then increases  $F$ . The most dramatic effect was generated by the addition of 1% or 2% 45 – 60 nm silica particles to 8 million g/mol PEO solutions, which leads to an almost complete cleanup (see figure 5).

Wang *et al.* 2004 showed that the resistance of the macromolecular solution to shear and extension increases with nanoparticle concentration but the increase of resistance in extension is much greater than its increase in shear.

### II.3 Particle laden tubeless siphon (non colloidal inert particles)

The experiments of Wang & Joseph 2003 showed that seeding of PEO solutions with inert, non

colloidal, neutrally buoyant particles in the submillimeter range gives rise to exceptional siphoning properties similar to those seen in “nanosiphons”. Click on movies of the experiments can be found at <http://www.aem.umn.edu/people/faculty/joseph/cleanup>.

Filaments of high molecular weight polymeric solutions can support very high extensional stresses without breaking: a fluid is sucked through a nozzle with the nozzle elevated above the surface of the liquid. Instead of the liquid breaking as in unthickened (Newtonian) liquids like water, glycerin or oil, an unsupported fluid column is drawn from a pool below into the nozzle above without breaking as shown in figures 8.

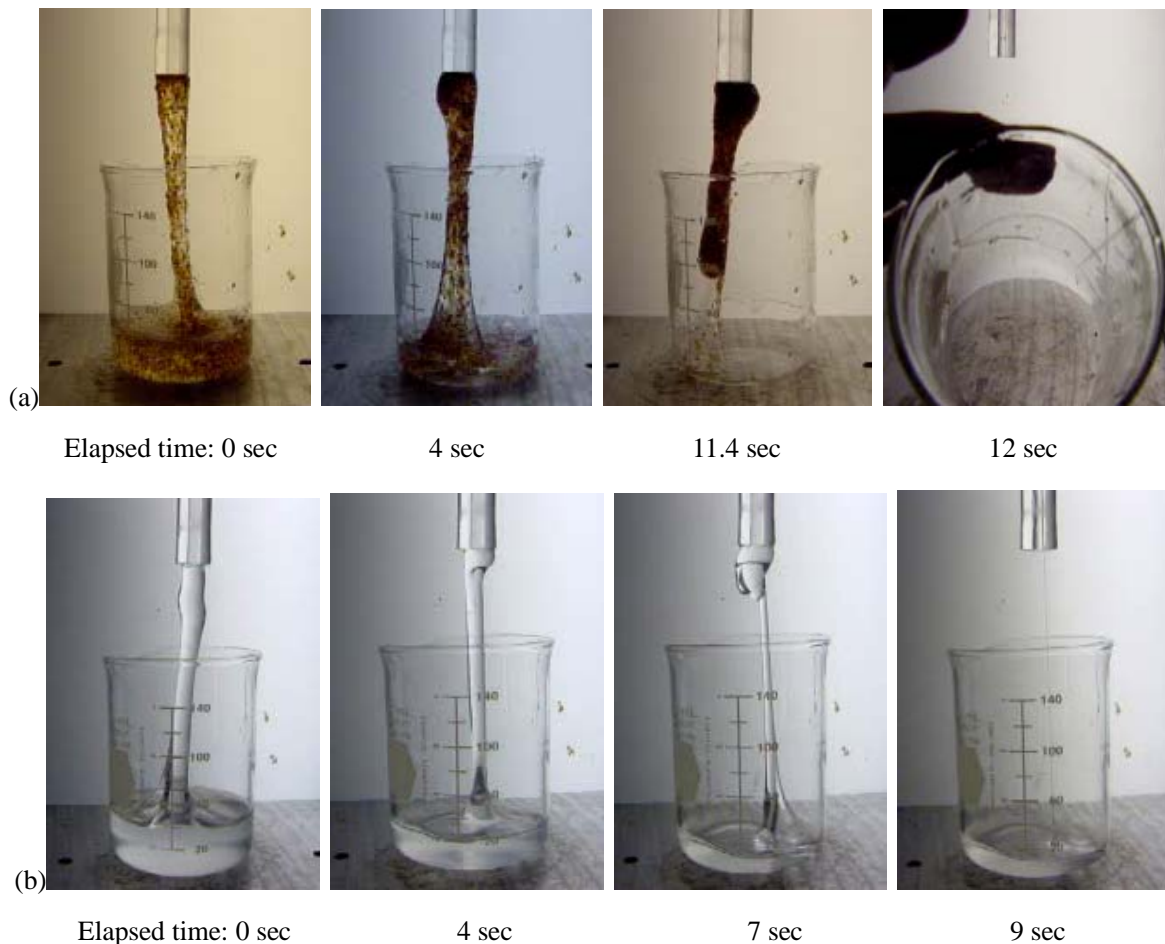


Figure 8. Comparison of tubeless siphons with particles (a) and without particles (b) of a 1% aqueous PEO solution at a suction speed of 0.052 cm/s. (a) The siphon is loaded with 4% by volume of 850  $\mu\text{m}$  resin particles. All the mixture is cleaned from the beaker. (b) When there are no particles, a puddle of fluid is left in the beaker. The same container is used in case (a) and (b); the initial volume of the fluid-particle mixture in (a) is equal to the initial volume of the fluid in (b).

The thickened (viscoelastic) liquids may be sucked from a substrate remotely with a “vacuum cleaner”. The emptying fraction  $F$ , defined as the ratio of the volume sucked out to the initial volume, is a function of the controlling parameters such as the suction speed, the particle size and concentration, the rheological parameters of the liquid, the nozzle size, the temperature, and the surface roughness of the substrate.

The problem of complete cleaning ( $F = 1.0$ ) was not studied before the recent work of Wang & Joseph 2003. They found that the emptying fraction increases rapidly as the suction speed increases; above a certain threshold speed, the liquid can be completely cleaned from a substrate (see figure 9 where the emptying fraction  $F$  vs. suction speed  $U$  curves are plotted). They also found that the addition of sub-millimeter solid particles in modest concentrations (<10% by volume) to the polymeric solutions can greatly enhance the pulling power and reduce the threshold suction speed required for a complete cleaning (see figure 8). Under certain circumstances, for example, when the suction speed is very low,



complete cleaning cannot be achieved even with particles added; instead, a maximum emptying fraction  $F_m < 1$  is reached in a certain range of particle concentrations (see figure 9(b)).

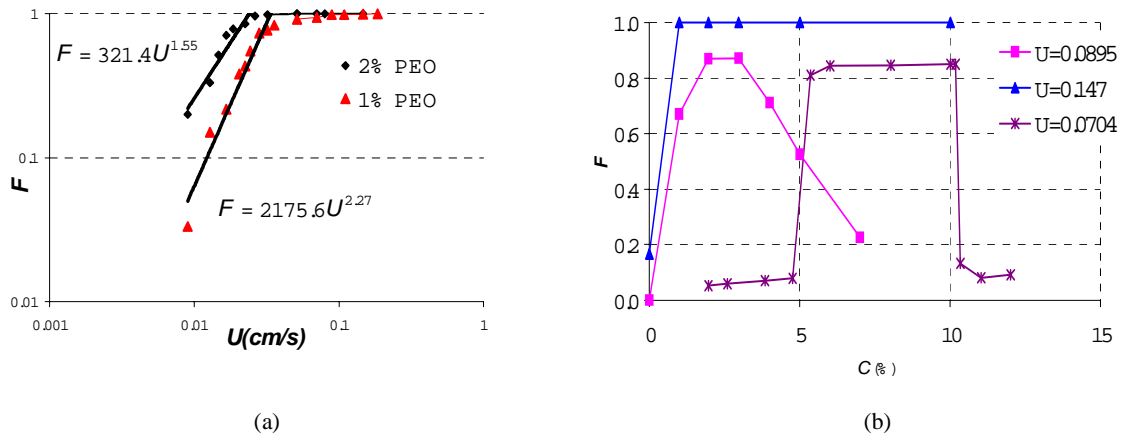


Figure 9. (a) Emptying fraction  $F$  vs. suction speed  $U$  for 1% and 2% aqueous PEO solutions. (b) The suction fraction  $F$  vs. the concentration of particles  $C < 12\%$  in a 1% aqueous PEO solution. Suction speed  $U = 0.0704$ ,  $0.0895$ , and  $0.147$  cm/s. When  $U = 0.147$  cm/s, the presence of particles in the solution increases the suction fraction dramatically and complete cleaning is achieved at about 1% particle concentration. When  $U = 0.0704$  or  $0.0895$  cm/s, the suction fraction first increases then decreases with the particle concentration; complete cleaning is not observed, instead a maximum suction fraction  $F_m < 1$  is reached in a certain range of particle concentrations.

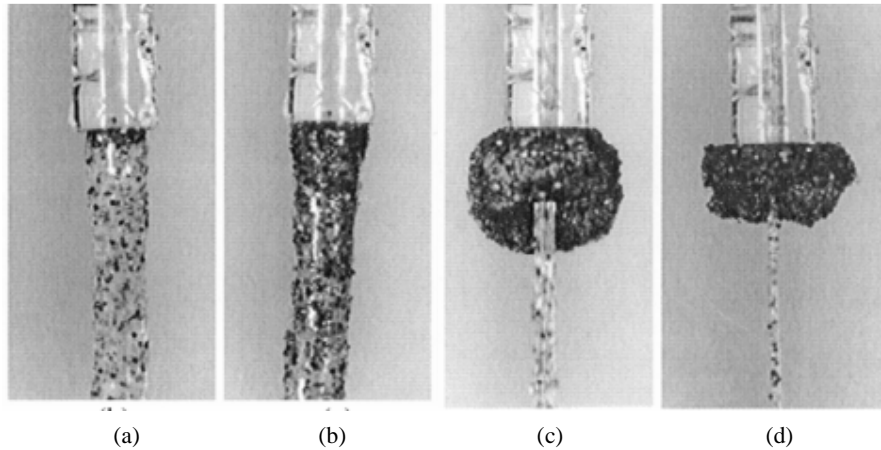


Figure 10. Photos for siphon experiments using brown resin particles. In (a) and (b) nearly all the particles are filtered out and do not enter the nozzle. In (c) and (d) a cluster of particles is around the nozzle and the siphon continues even though the fluid column has a smaller radius than the tube.

The mechanism of the particle laden tubeless siphon is not well understood but is probably related to the screening of particles in the siphon. The photographs in figure 10 show that particles are brought up by the siphon but filtered out at the nozzle; almost none of them enter the tube. As the siphon proceeds, more and more particles accumulate near the nozzle and a cluster of particles can often be seen around the nozzle (see figures 10(c) and (d)). When the volume of fluid left in the beaker decreases, the fluid column will neck down at the nozzle so that the cross-sectional area of the liquid column is smaller than the cross-sectional area of the nozzle; air will be sucked in and the liquid column ruptures, stopping the siphon. However, the presence of the cluster of particles around the nozzle can prevent air from entering the nozzle. Thus, the presence of the particles prolongs the time of the siphon process and helps the suction. The clustering of the particles could be explained by the reversal of the sign of the normal

stresses at stagnation points on the particles, which follows from a viscoelastic potential flow analysis of a second order fluid past an sphere (see Section V for more detail of the analysis).

In addition to this clustering, we believe that the addition of particles to the PEO solution also leads to a stress field that produces “mechanical” bonds between the macromolecules. These “bonds” are really hydrodynamic forces that cause the motion of different macromolecules to become highly coupled. In this way, a large composite macromolecule is created and the resulting solution has enormous extensional stresses and exceptional siphoning properties. We propose to investigate this idea through direct numerical simulations of particle motion in viscoelastic fluids.

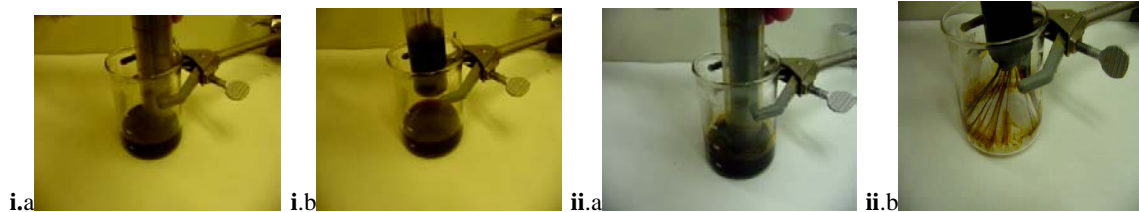
## II.4 Cleanup

The experiments on tubeless siphons laden with nanoparticles (figure 3) and with inert, noncolloidal submillimeter particles (figure 8), terminate in complete cleanup ( $F=1$ ) of the beaker. This cleanup which is exhibited in the figures, is much clearer in the actual experiments shown in movies on our websites <http://www.aem.umn.edu/people/faculty/joseph/particles/nano/index1.html>.

The beaker may be cleaned without particles, but it takes a much larger velocity  $U$  of the piston to reach complete cleaning  $F=1$ . The polymer solutions with and without particles are extensional thickening; they get stiffer and stiffer with the rate of extension. This stiffening is enhanced by the presence of particles, especially nanoparticles. The panel at  $t=27$  in figure 3, shows that the liquid is peeled off the pyrex glass substrate. The peeling is something like an adhesive tape; however the precise nature of the peeling is determined by the balance of peeling forces and the forces of adhesion which depend on the liquid and solid substrate. The final stage of cleanup always takes place with the formation of stiffened viscoelastic filaments which pull the liquid filaments from the substrate like spiderman.

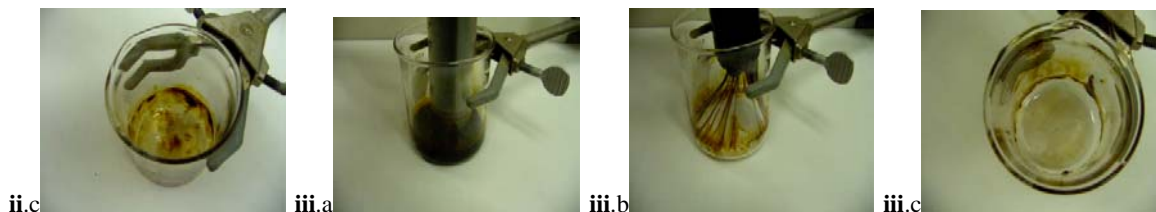
Similar experiments demonstrating effective cleaning by sucking off high molecular polymeric liquids were done with oil rather than water-based solvents. These experiments were motivated by the idea that if solid substrates could be cleaned by pulling off thickened liquids, preferably laden with particles, the same could be done with oil slicks. A commercial product *Elastol* which is effective for cleaning oil slicks is used in just this way. *Elastol* is a high molecular weight polymer which may be mixed with oil for oil slick removal. *Elastol* is in liquid and powder form. We did some preliminary experiments to show that this product can be improved by addition of solid particles. A hand held piston with a piston-sucking device is used to demonstrate that the oil can not be removed without additives, that it can be removed when a small amount of elastol is added and that the addition of particles leads to still better cleaning (see figure 11, the movies is at

<http://www.aem.umn.edu/people/faculty/joseph/cleanup>). Panels ii.b and iii.b show the spider-web like structure which occurs at the final stage of cleaning.



*i. Movie: suction of oil.*

*ii. Movie: suction of the oil-Elastol mixture.*



*iii. Movie: suction of the oil-Elastol mixture laden with particles.*

Figure 11. Three attempts to clean a substrate covered with oil. *i.* Oil is in the substrate and it cannot be sucked out because the oil breaks. *ii.* A small amount of Elastol is added to the oil (say 5%) and the oil-Elastol mixture can be pulled out but the bottom of the substrate is slightly soiled with oil. *iii.* Particles are added to the oil-Elastol mixture. The particles are sub-millimeter and nearly neutrally buoyant. The particles are not special, they are polydisperse and not spheres. The Elastol-oil-particle mixture is pulled out of the beaker; the bottom of the beaker is cleaned.

It is well known that elastol additives are effective in remediating oil slicks. It is true, but not known, that the addition of small particles to the elastol improves the cleaning action of the additives (see <http://www.aem.umn.edu/people/faculty/joseph/cleanup/>)

A fundamental aspect in the study of cleanup is the problem of adherence. There is a bonding strength between a given fluid and solid substrate which must be overcome by the pulling power of viscoelastic threads stiffened by high rates of extension.

Given a substrate and a fluid we may study the dynamics of cleanup. We are interested in how stiffened polymer solutions are pulled off the substrate at high rates of extension. This study can be done with tubeless siphons and with hand held devices which operate with a piston and cylinder as is the case with tubeless siphons. These devices operate by pulling rather than by pressure differences; they may be used like a vacuum cleaner to remove thickened liquids from substrates on which they have been spread for cleaning. It is proposed to test the power of these stiffened liquids to remove contaminants from contaminated surfaces. In the fundamental studies we would compare cleanup solutions with polymers, with polymers plus particles and particles plus nanoparticles. The goals of cleanup studies are to understand the removal of liquids from substrates at high rates of pulling and to study the practical potential of this method as a practical method for the removal of contaminants from substrates.

### III. DEGRADATION

It is well known that PEO can be easily degraded by oxidative attack, and this degradation can be accelerated in the presence of heavy metal ions, oxidizing agents, strong acids, and radiation (McGary 1960; Duval & Sarazin 2003). If a bottle of PEO solution is left at room temperature for over a month, it will become almost Newtonian. We noticed that the presence of silica nanoparticles seemed to slow down the degradation of PEO. In table 4, we compare the emptying fraction  $F$  in open siphon experiments using fresh PEO/silica suspensions with using aged suspensions.

PEO MW (g/mol)	PEO (wt %)	Silica (wt %)	Silica size (nm)	$F$ (fresh suspension)	$F$ (aged suspension)	aging time (days)
8 million	0.5	0.5	10 – 20	20.8%	1%	60
		1.0		62.5%	60.4%	60
		2.0		87.5%	73.0%	60
		0.5	45 – 60	92.5%	89.5%	30
		1.0		98.3%	98.2%	30
		2.0		99.1%	99.1%	60
4 million	0.5	0.5	45 – 60	70.6%	22.9%	50
		1.0		89.1%	47.9%	45

Table 4. A comparison of the emptying fraction  $F$  using fresh PEO/silica suspensions with using the same suspensions left at the room temperature for a period of time. The tilting angle in these experiments is  $15^\circ$  and the initial height of the siphon column  $h_1$  is 42.3 cm. The PEO concentration in these samples is 0.5%.

From table 4, one can see that suspensions with only 0.5% silica particles show severe degradation, whereas the degradation of suspensions with 1% or 2% silica particles is much less severe. Particularly, the 8 million g/mol 0.5 wt% PEO solution laden with 1% or 2% 45 – 60 nm silica particles shows almost no degradation, as measured in the open siphon experiments. At present, there is no explanation of this effect; apparently PEO molecules bonded with silica particles are less liable to oxidative attack. It is possible that the nanoparticles absorb precisely on the oxidation site and block the oxidation.

Studies of degradation can be carried out by repeated rheological testing on the same samples with and without nanoparticle (see section IV) and by structure studies using x-ray scattering (see section V).

### IV. RHEOLOGICAL STUDIES

It is necessary to test and compare polymer solutions with particle laden solutions and these with nanoparticle-polymer macromolecular solutions. Till now, we have worked with silica nanoparticles and PEO solutions with molecular weights of 4 and 8 million. We are proposing to look for other nanoparticle-polymer and solvent combinations with exceptional properties. Two candidates are polyacrylamide and silica nanoparticles and carbon nanotubes in oil solvents. As is the case with PEO solutions, the rapid degradation of polyacrylamide to oxidation may be blocked by nanoparticles.

Single wall nanotubes have a very particular hexagonal cell structure leading to very long tubes of great strength with high electrical and thermal conductivity. These tubes can be up to one hundred times as strong as steel; the diameter of these tubes is 1.2-1.4 nm with lengths as much as two microns. The density of such tubes is almost  $1.35 \text{ g/cm}^3$ . Single-wall nanotubes are similar to polymer chains; they can interact with polymer chains in intertwined ways that carbon fibers and even multi-wall nanotubes cannot.

Our interest is in creating suspensions with exceptional extensional properties using carbon nanotubes and polymer solutions. We have already noted that Hobbie *et al.* 2003 created a dispersion of multiwall carbon nanotubes in a solution of very high molecular weight polybutadiene in a solvent of very low molecular weight polybutadienes. Choi *et al.* 2001 created a colloidal dispersion of multiwall nanotubes in synthetic poly ( $\alpha$ -olefin) oil. This suspension exhibited high thermal conductivity; rheological properties were not measured. It is possible that a dispersion of carbon nanotube in liquids can have exceptional rheological properties even without polymers.

We propose to do the following rheological tests comparing polymer and nanoparticle-polymer solutions.

- (1) Filling fraction tests for the tubeless siphon
- (2) Shear stress vs. shear rate
- (3) Dynamic modulus vs. frequency
- (4) Shear wave speeds (Joseph *et al.* 1986)
- (5) Capillary thinning (see appendix by Mike Owens in Wang, Bai & Joseph 2004)

## V. SAXS & XPCS STUDIES OF NANOPARTICLE-PEO-WATER SOLUTIONS

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The addition of nanoparticles to polymeric solutions could change the molecular structures of the polymer in profound ways. The proposed filler networking mechanism where nanoparticles are bridged by polymer molecules should be tested by structure analysis. Present-day material characterization techniques enable nano-meter physical probes. Unfortunately, most of these can not be used for the watery solution of interest here. Two methods which can work for solutions are small angle x-ray scattering (SAXS), time-resolved SAXS and coherent small-angle x-ray photon correlation spectroscopy (XPCS) measurements of relevant silica-nanoparticle-PEO-water composites. Generally speaking, SAXS will provide information on the size and shape of the postulated composite macromolecules, time-resolved SAXS will generate insight into the microscopic nature of the reduced degradation of PEO and XPCS will yield data on the motion of the composite macromolecules.

### SAXS Studies of Silica-PEO-Water Solutions

SAXS provides information about the size and shape of particles in a host matrix. In this particular case, we are interested in whether silica nanoparticles and PEO form composite macromolecules or not. We will obtain this answer by performing SAXS measurements on a series of nanoparticle-PEO-water solutions varying from zero concentration of PEO to high concentrations of PEO. The corresponding observed effective particle form factors will provide microscopic *in situ* determination of whether PEO adheres to the silica nanoparticles. It will also allow us to address the similar question of whether the silica particles aggregate. We note that the size range of the silica nanoparticles (and the expected size ranges of the composite macromolecules) is ideally suited to the preeminent SAXS capabilities of Beamline 8-ID at the Advanced Photon Source.

## Time-Resolved SAXS Studies of Silica-PEO-Water Solutions

Additional information about the silica-PEO-water solutions can be obtained by extending our SAXS measurements into the time domain. In the near term, we plan to investigate the microscopic characteristics of the decreased degradation observed for nanoparticle-enhanced PEO-water mixtures. With time-resolved SAXS we can straightforwardly determine whether the composite properties remain static with time and, if not, the microscopic nature of the observed changes. In the medium term, we plan to enhance the capabilities of Beamline 8-ID by developing a shear cell that will permit SAXS studies of materials under applied stresses. Such a capability will allow us to microscopically relate the microscopic morphological properties of the composite to the rheological properties that will be investigated as part of this proposal. Once again, we note that these type of studies correspond exactly to capabilities provided by Beamline 8-ID.

Polymer solutions degrade strongly under x-ray. Solutions with and without nanoparticles may be tested for degradation due to x-rays.

## XPCS Measurements of Silica-PEO-Water Solutions

XPCS is an emerging technique at high-brilliance synchrotron beamlines, such as IMMY/XOR-CAT Beamline 8-ID at the Advanced Photon Source (APS), for studying dynamic phenomena in materials at a combination of length and time scales that are inaccessible to other experimental techniques. XPCS is the x-ray analog of the laser-light PCS method (also known as dynamic light scattering or DLS). Specifically, by illuminating the sample under study with a (partially) coherent beam of electromagnetic radiation, the PCS method reveals the characteristic fluctuation times of the sample via auto-correlation of its speckled scattering pattern. XPCS has proven effective at measuring the dynamics of nano-sized particles in fluids (Liu & Joseph, 1993; Leal, 1975; Chiba *et al.* 1986) and polymer and block copolymer dynamics (Cho *et al.* 1992; Riddle *et al.* 1977). This unique technique promises to be especially relevant to the key question regarding nanoparticle enhanced siphoning of PEO-water mixtures: are the silica nanoparticles bridged or not? Using XPCS, the answer will be straightforward: bridged silica nanoparticles will show non-decaying or very slowly decaying autocorrelation functions while non-bridged silica nanoparticles will not. Moreover, in the situation where a fraction of the nanoparticles are bridged and the remaining fraction is not, the autocorrelation function will either show multiple decays or decreased initial amplitude. In all cases, XPCS will reveal the detailed dynamic morphology of the solutions.

## RHOLOGY AND SAXS STUDIES

Wang and Lodge 2002 investigated the Cylinder-to-Gyroid transition in a block copolymer solution using a combination of rheology and small-angle X-ray scattering (SAXS). Figure 12 shows the rheology data and the corresponding SAXS patterns from their study. Our aim is to study the nanometer-scale structure of polymeric solutions laden with nanoparticles when they are subject to extension. Nanometer-scale characterization may reveal rich and novel structures arising from polymer-nanoparticle interactions and effects of extensional stresses. Our research is one realization of the opportunities to construct new fluid materials with special properties as a composition of nanoparticle and polymeric solutions.

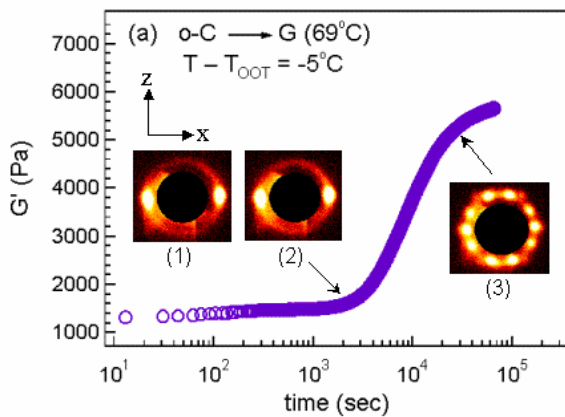


Figure 12. Evolution of  $G'$  compared to the corresponding SAXS patterns for a "shallow" quench from o-C (Wang and Lodge 2002).

## VI. FLOW INDUCED MICROSTRUCTURE

There is a very strong tendency for particles to aggregate in the motions of viscoelastic fluid with stronger aggregation in more elastic polymer solutions. This tendency is encountered for particles of all sizes (from microns to centimeters) and in different kinds of motion.

- (1) Shear flow [13-15]
- (2) Extensional flow [13, 17]
- (3) Sedimentation [1, 18]
- (4) Fluidization

The tendency to aggregate is strong and robust. It is definitely a property of viscoelastic fluids; the same particles disperse rather than aggregate in Newtonian fluids.

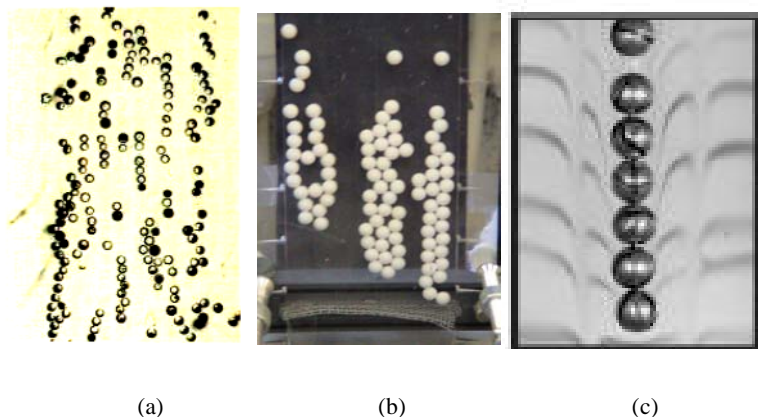


Figure 13. Flow induced microstructure. Spheres line up in the direction of flow (a) Extensional flow [13], (b) Sedimentation and (c) fluidization in a 1% aqueous PEO solution.

The aggregates that form in the flows of polymeric solutions are usually chains of spheres, all in a row, held together strongly by fluid forces, viscoelastic pressures associated with shears and possible tensions at points of stagnation. Aggregates of particles which are not chains, appear to be assemblies of chained particles (Joseph 2002; Hobbie *et al.* 2003; Joseph 1996). The alignment and chaining of spheres in elongation is possibly an important mechanism underlying the unusual response of tubeless siphons to the addition of inert submillimeter particles in moderate concentration.

The fact that small particles appear to aggregate in all these different kinds of flows suggests that universal principles are involved. It is important to determine which features are universal and what are the differences. In our studies of sedimentation and fluidization, we have found that the microstructural arrangements of spherical particles are controlled by the stable orientation of long particles (Leal 1975; Chiba 1986; Cho *et al.* 1992; Joseph 1996). The tendency of particles to chain in the direction of flow may also simply that the stable orientation of long bodies in these flows are also along the stream.

## VII. RESEARCH SUMMARY

- Characterize and correlate flow properties, and cleanup properties with the rheology and molecular structure of solutions of polymers, polymers plus inert particles and polymers plus nanoparticles in water.
- Study degradation by oxidation in the nanoparticle solutions by repeated testing of the same samples of polymeric solutions with and without nanoparticle.
- Study the structure of the nanoparticle solution using X-ray scattering and related techniques. Correlate these studies with siphon behavior and rheological measurements.
- Do rheological modeling, mathematical and numerical analysis to illuminate the mechanical foundations of exceptional siphon behavior and cleaning properties in the similarity between nanosiphons and particle-laden tubeless fortuitous or fundamental.

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