Anisotropic Nanoparticles Contributing to Shear-Thickening Behavior of Fumed Silica Suspensions

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Supporting Information

ABSTRACT: Rheological characteristics of a concentrated suspension can be tuned using anisotropic particles having various shapes and sizes. Here, the role of anisotropic nanoparticles, such as surface-functionalized multiwall carbon nanotubes (MWNTs) and graphene oxide nanoplatelets (GONPs), on the rheological behavior of fumed silica suspensions in poly(ethylene glycol) (PEG) is investigated. In these mixed-particle suspensions, the concentrations of MWNTs and GONPs are much lower than the fumed silica concentration. The suspensions are stable, and hydrogen-bonded PEG solvation layers around the particles inhibit their flocculation. Fumed silica suspensions over the concentration range considered here display shear-thickening behavior. However, for a larger concentration of MWNTs and with increasing aspect ratios, the shear-thickening behavior diminishes. In contrast, a distinct shear-thickening response has been observed for the GONP-containing suspensions for similar mass fractions (MFs) of MWNTs. For these suspensions, shear thickening is achieved at a lower solid MFs compared to the suspensions consisting of only fumed silica. A significant weight reduction of shear-thickening fluids that can be achieved by this approach is beneficial for many applications. Our results provide guiding principles for controlling the rheological behavior of mixed-particle systems relevant in many fields.

INTRODUCTION

Concentrated suspensions are found in consumer products and in many manufacturing processes.1,2 The flow behavior of these suspensions depends on factors such as size and shape of the suspended particles, particle concentration and surface chemistry, and the interaction between the particles and suspending media.3–6 All of these factors in combination dictate the rheological behavior of the fluids, including shear rate-dependent viscosity behavior demonstrated by shear-thinning and shear-thickening responses, yield stress, elasticity, etc.7,8 In shear-thickening fluids (STFs), viscosity increases abruptly beyond a critical shear rate (γ_c).9,10 In drilling fluids, the shear-thickening behavior is detrimental.11 In contrast, such responses can be beneficially harnessed for applications including the enhancement in ballistic and stab resistance of personal body armor,12 vibration damping of skis and tennis rackets,12 and spacecraft shielding.13

A number of earlier investigations on STFs considered suspensions of high-volume-fraction spherical silica particles.14–17 For STFs, as rationalized for spherical particles, the viscosity increase beyond a critical shear rate has been attributed to the formation of transient, stress-bearing hydroclusters.9 Subjected to shear flow, the particles in concentrated suspensions can come close together as the suspending fluid between the particles is displaced. The hydrodynamic force (F_hydrodynamic) between two particles is inversely proportional to the separation distance between them, for example, the hydrodynamic force between two spherical particles of radius a separated by a distance h is F_hydrodynamic = 6πη a^3γ / h. Here, η is the viscosity of the suspending media and γ is the shear rate.14,18 On the other hand, the Brownian motion of the particles and the repulsive forces caused by solvation layer compression as the particles approach will deter the particles from coming closer together. At γ_c, the attractive and repulsive forces become equal and multiple particles in closed orbits form hydroclusters. Beyond γ_c, the hydroclusters start to grow and an increase in viscosity (shear-thickening) is observed.16,17,19 Hydrocluster formation has been simulated9,20 and investigated experimentally.21–23 These studies predict that hydroclusters form oriented along the shear plane’s compression axis.20,24 Both experimental and simulation studies have also captured friction-induced clustering of particles with rough surfaces.10,25,26 However, particles with solvation layers (as discussed below) may not experience significant friction. Because the hydroclusters/clusters are not bonded physically or chemically, they dissociate as the flow is removed. Thus, the shear-thickening response is mostly reversible.16

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Continuous, gradual shear thickening with spherical particles can be changed to discontinuous, rapid shear thickening through the addition of low volume fractions of anisotropic particles. For example, fractal fumed silica particles display distinct shear-thickening behavior at a very low mass fraction (MF) of 0.05 in poly(propylene glycol). Mixing and processing of these lower-mass/volume-fraction suspensions are relatively easy in comparison to high-volume-fraction suspensions. Lower solid content also results in the addition of low volume fractions of anisotropic particles with high aspect ratios have also been considered, including multiwall carbon nanotubes (MWNTs), accicular precipitated calcium carbonate (PCC) particles, rod-shaped silicon carbide whiskers, cubic aluminosilicate zeolite, and carbon black/alumina suspensions. The aspect ratio of PCC was shown to play no role on the critical shear stress for shear thickening but affected the transition from continuous to discontinuous shear thickening. Rheo-small angle neutron scattering results indicated that flow-oriented particle structure was mostly maintained throughout shearing. MWNTs with larger aspect ratios than PCC display shear thickening in N-methyl-2-pyrrolidone. These particles were not surface-functionalyzed, so shear thickening was induced by flocculation rather than by hydroclustering. Interestingly, the flocculated fumed silica particles did not shear-thicken, but gel formation was observed.

Particle interactions with the dispersing medium (mostly the secondary bonding) is another important factor. For example, hydrophilic fumed silica forms hydrogen bonds to poly-(ethylene glycol) (PEG), resulting in a well-dispersed, nonflocculating system, which is very stable. The characteristic time scale for association and dissociation of hydrogen bonding is faster than the deformation time scale. As the particles come close, the entropic penalty associated with the solvation layer compression plays an important role in shear thickening. Shear thickening of hydrophilic fumed silica nanoparticles in ionic liquids and ionic structure effects on suspension viscoelasticity have also been investigated experimentally. Such experiments revealed shear-thickening behavior by hydrophilic ionic liquids, whereas gel formation occurred in hydrophobic liquids, displaying shear thinning at high shear rates.

Mixed-particle systems have been investigated to help in tailoring shear-thickening responses. In these systems, the concentration of primary particle is much higher than that of the other (secondary) particle. Sha et al. showed that both nonfunctionalized graphene nanoplatelets (GNNPs) and MWNTs, when added as secondary particles, alter the shear-thickening behavior of 75 wt % spherical (650 nm) silica nanoparticle PEG suspensions. Adding either 1–3 wt % of GNNPs or MWNTs to silica suspensions resulted in lower critical shear rates for shear thickening versus the suspensions with only silica particles. Another study revealed that adding nonfunctionalized MWNTs to high-weight-fraction (~44 wt %) fumed silica suspensions in PEG decreased viscosity and increased critical shear rate, contrary to the report by Sha et al. Non-surface-functionalized MWNTs and GNNPs can flocculate in polar PEG, so mixing those in suspensions containing high MFs of silica can be a challenge. Stability of these suspensions can also be poor due to the large silica particles and the absence of hydrogen bonding between the particles and PEG. In another study, a surfactant was used to disperse MWNTs in a silica–ethylene glycol suspension to obtain a stable suspension. Here, the silica particle content was high (~64 wt %). These particles were of irregular shape with an average size of 2 μm. The shear thickening improved with the addition of MWNTs, although the concentration of nanotubes was low compared to other reports and our current study. Nanotubes were postulated to form a network, restricting the SiO₂ particle motion, leading to shear thickening.

Hydroclustering in a mixed-particle system can depend on the difference in shape between the primary and secondary particles and on their size ratio. Hypothetically, to obtain maximum shear-thickening behavior, the particles pack closely along the compression axis. Secondary particles that are larger than the primary particles may not orient along the compression axis and hinder hydroclustering formation. Results from mixed-particle systems can also be compared to the bimodal suspensions consisting of spherical particles with two different diameters. Increasing the mass fraction of small particles relative to the larger particles enhances shear thickening and increases the critical shear stress.

In this study, MWNTs functionalized with surface-hydroxyl functional groups or graphene oxide nanoplatelets (GNNPs) were added independently into fumed silica suspensions in PEG. The goals were to elucidate the effect of anisotropic carbon nanoparticles on the shear-thickening behavior of concentrated suspensions and to examine the contradicting results in the literature. The suspensions prepared here were

| samples                           | MF of A200 silica | VF of A200 silica | MF of MWNT or GONPs | VF of MWNT or GONPs |
|-----------------------------------|------------------|------------------|---------------------|---------------------|
| PEG                               | N/A              | N/A              | N/A                 | N/A                 |
| PEG + 0.02 MF S-MWNTs             | N/A              | 0.02             | 0.015               | 0.008               |
| PEG + 0.015 MF S-MWNTs            | N/A              | 0.02             | 0.015               | 0.008               |
| PEG + 0.02 MF GONPs              | N/A              | 0.02             | 0.015               | 0.008               |
| PEG + fumed silica                | 0.15             | 0.0820           | N/A                 | N/A                 |
| PEG + fumed silica + 0.002 MF S-MWNTs | 0.15             | 0.0821           | 0.002               | 0.0012               |
| PEG + fumed silica + 0.01 MF S-MWNTs | 0.15             | 0.0822           | 0.01                 | 0.0058               |
| PEG + fumed silica + 0.02 MF S-MWNTs | 0.15             | 0.0829           | 0.02                 | 0.0117               |
| PEG + fumed silica + 0.002 MF L-MWNTs | 0.15             | 0.0821           | 0.002               | 0.0012               |
| PEG + fumed silica + 0.01 MF L-MWNTs | 0.15             | 0.0822           | 0.01                 | 0.0058               |
| PEG + fumed silica + 0.015 MF L-MWNTs | 0.15             | 0.0826           | 0.015               | 0.0087               |
| PEG + fumed silica + 0.01 MF GONPs | 0.15             | 0.0825           | 0.01                 | 0.0054               |
| PEG + fumed silica + 0.02 MF GONPs | 0.15             | 0.0829           | 0.02                 | 0.0109               |
well dispersed and were stable over a prolonged duration versus those of nonfunctionalized nanoparticles. Hydrogen bonding between the particles and PEG stabilizes the suspensions. The onset and slope of shear thickening strongly depend on the nanoparticles’ MF and shape. We have shown that for the nanotube-containing suspensions the shear-thickening behavior gradually disappeared with the increasing concentration of nanotubes. In contrast, over the concentration range investigated here, GONPs enhance the shear-thickening behavior of fumed silica suspensions. We attempted to elucidate the mechanism behind such shear-thickening behavior.

Our study was also motivated by the fact that carbon nanoparticles can alter the electrical and thermal transport properties of suspensions. These important properties can be a function of the applied shear rate and the corresponding structural evolution. Although investigations on the mixed-particle system are not common, change of electrical conductivity in nanoparticle suspensions has been widely reported. Improved understanding of the flow behavior as investigated here can lead to a better control of mixed-particle system transport properties. Potential applications exist in multifunctional composites. Results from this study provide new understanding regarding the rheological behavior of concentrated suspensions of mixed-particle systems having applications in many fields.

■ RESULTS AND DISCUSSION

MWNT dispersions were prepared by mixing various MFs of short MWNT (S-MWNT) and long MWNTs (L-MWNT) in PEG 200. Sample compositions, including the MF and volume fraction (VF) of A200 silica, MWNT, and GONP, are shown in Table 1.

Characterization of Nanoparticles. GONPs were characterized using atomic force microscopy (AFM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). TEM and AFM images (Figures S1 and S2) show that the GONPs have lateral dimensions in the range of 500 nm to 1 μm versus thicknesses from 1.1 to 2.6 nm, signifying that only two to three graphene layers are present in the GONPs. Considering width, W ≈ 500 nm, and thickness, T ≈ 1.1–2.6 nm, the GONP aspect ratio ranges from ~200 to 500. The interlayer spacing between graphene plates is representative of the oxidation level. The XRD data (Figure S3) confirmed that the basal plane spacing increased from graphite’s value of 0.34 to 0.93 nm for GONPs. XPS analysis of GONP samples determined the level of oxidation. Both low and curve-resolved high-resolution (HR) spectra are shown in Figure S4. The HR spectrum was deconvoluted to determine the existence of different functional groups and their relative quantities. These synthesized GONPs consist of about 51% oxidized carbon and 49% graphitic carbon with the following order of abundance of oxygen functional groups C==O > C−O > O−C==O (Figure S4).

The TEM image (Figure 1a) of A200 silica exhibits loosely interconnected branched aggregates of ~12 nm diameter primary particles fused together in fractal structures (100–200 nm), as previously reported. The surface area of A200 silica is ~200 m²/g. This surface is covered with both isolated and bridged silanol groups with densities of ~1.15 and ~1.5 nm⁻², respectively.

S-MWNTs with lengths of 0.5–2 μm and L-MWNTs with lengths of 10–30 μm were used in this study. Both types of MWNTs had outer and inner diameters (D) of 10–20 nm and 3–5 nm, respectively. The aspect ratios (L/D) for the MWNTs varied from 25 to 200 for the short tubes and from 500 to 3000 for the long tubes. The supplier-provided specific surface area is 233 m²/g for the MWNT samples. Using a 3–4 wt % OH content in these MWNTs (provided by the supplier), the OH group surface density was estimated to be ~4.56 nm⁻². Furthermore, on the basis of the dimensions of GONPs, we have estimated the surface area to be ~500 m²/g. Short nanotubes (0.015 MF) intermingled with silica surfaces (0.15 MF) are shown in Figure 1b. In contrast, evidence of silica particle aggregation on GONP surfaces likely due to hydrogen bonding between GONPs and fumed silica as ethanol dried during sample preparation can be seen in Figure 1c (also see Figure S5). During high-shear mixing, the particles become well dispersed in PEG 200. These suspensions are stable for a prolonged duration, and no phase separation has been observed for weeks in stored samples.

Molecular Interactions. The surface chemistry of these MWNTs and GONPs plays a significant role on the rheological responses due to their large surface areas. The hydroxyl group surface density on the MWNTs (~4.56 nm⁻²) is approximately twice that of the silanol groups on A200 silica. Similarly, the hydroxyl, ketone, epoxy, and carboxylic group surface densities on the GONPs are ~5.33 nm⁻². These functions can readily hydrogen-bond to the silanol groups on A200 silica surfaces and to the ether and terminated hydroxyl groups of PEG.

Fourier transform infrared (FTIR) spectra exhibited OH stretching of PEG at 3411 cm⁻¹, which shifted toward lower wavenumbers of 3400, 3399, and 3396 with the addition of fumed silica, GONPs, and S-MWNTs, respectively. This confirmed enhanced hydrogen bonding occurred between
PEG and silanol groups of fumed silica and/or surface functional groups (carboxylic/hydroxyl/ether) of nanoparticles (Figure S6). Hydrogen bonding between PEG and silanol groups of fumed silica particles has also been reported in the literature as the peak at ~3400 cm$^{-1}$ shifts toward lower wavenumbers. Hydrogen-bonded PEG around the particles results in a solvation layer around the particles. Without this solvation layer, flocculation of silica nanoparticles can take place, as observed in a system where the PEG molecules were end-capped with methyl groups. A PEG solvation layer also hinders nanotube and GONP flocculation similar to fumed silica, i.e., the nanoparticles will not undergo significant hydrogen bonding within themselves, which promotes aggregation or flocculation. The fully stretched length of PEG 200 is ~1.8 nm; therefore, the minimum thickness of the solvated layer can be considered to be of the same order.

**Rheological Investigations.** The effect of suspended particle shape and size on rheological responses was investigated by examining the steady shear and dynamic rheology of PEG suspensions containing MWNTs and GONPs. The low shear viscosity for the S-MWNT suspension was found to be slightly higher than that for the same MF of GONPs; however, the high-shear-rate values were similar.

Figure 2b represents storage moduli ($G'$) and loss moduli ($G''$) for the same suspensions as a function of applied strain amplitude. PEG 200's very low moduli could not be captured because of measurement limitation of our rheometer. The nature of suspended particles plays a role in the dynamic rheology responses similar to steady shear rheology results. At low strain amplitude, both $G'$ and $G''$ were independent of the applied strain amplitude in the linear viscoelastic region (LVE) for all samples. However, a decrease in $G'$ and $G''$ was observed beyond a critical strain, i.e., the samples strain-soften. In general, in the LVE region, $G'$ was almost an order of magnitude higher than $G''$ for both L- and S-MWNT suspensions. At higher strain values, a crossover was observed, where $G''$ became higher than $G'$. The low strain modulus for the L-MWNT suspension was larger than that of the S-MWNT suspension. For the GONP suspension, $G''$ is slightly higher than $G'$ in the LVE region. Interestingly, the critical strain corresponding to crossover (strain-softening behavior) was lower for S-MWNT and L-MWNT than for GONP suspensions. The yield stress values are 30, 4, and 1.4 Pa for L-MWNT, S-MWNT, and GONP suspensions, respectively (Figure 2c).

At low strain for the nanotube suspensions, $G' > G''$, indicating a soft solidlike behavior (Figure 2b). This is likely due to temporary network formation caused by nanotube entanglement or topological constraints. Similar network structures have been reported for SWNTs in high-molecular-weight PEG and MWNTs in low-molecular-mass polyisobutylene. The temporary network structure dissociates at higher stress/strain, as displayed by the yield stress. A higher yield stress in long tube suspensions versus short tubes indicates a stronger network structure in the former. As the structure yields at higher strain amplitude, the viscous response exceeds the elastic response. Interestingly, the viscosity versus shear rate data of MWNT suspensions (Figure 2a), particularly, at high MF, has some resemblance to the viscosity behavior of nematic liquid crystalline materials, i.e., three regions in viscosity versus
shear rate curves.\textsuperscript{2,53,54} For 0.02 MF S-MWNT and 0.015 MF L-MWNT suspensions, the rod number densities ($\nu$) are $\approx 2.9 \times 10^{13}$ and $1.4 \times 10^{12}$ cm$^{-3}$, respectively; $\nu$ is of the same order of $\approx 3 \times 10^{13}$ cm$^{-3}$ for S-MWNTs and more than $\approx 1.25 \times 10^{11}$ cm$^{-3}$ for L-MWNTs. Here, $L$ and $d$ are the average tube length and diameter, respectively. On the basis of Doi’s theory, the formation of a nematic liquid crystalline state is expected at this concentration.\textsuperscript{2} However, the 0.02 MF S-MWNT suspension did not display clear birefringent domains under cross-polar microscopy, which is typical for liquid crystals. Nanotubes in our samples have not been highly purified and have significant polydispersity. In addition, a small amount of agglomerates of nanotubes can be present in the sample. Therefore, polydispersity and agglomeration, if any, likely have hindered the formation of a liquid crystalline phase,\textsuperscript{55} although the rheological response has some signature of liquid crystals.\textsuperscript{56–59} A small degree of shear-thinning behavior was observed (Figure 2a) similar to that observed for GONP water suspensions.\textsuperscript{60}

As described previously, PEG-containing nanoparticles displayed interesting rheological behavior. Next, the effects of added nanoparticles on the rheology of silica suspensions were investigated and compared to the results for suspensions containing only fumed silica in PEG.\textsuperscript{14} Figure 3a,b displays the viscosity versus shear rate plots of 0.15 MF silica suspensions containing different MFs of S-MWNT and L-MWNT, respectively. The increase in viscosity associated with the addition of S-MWNTs (Figure 3a) is slightly lower than that with L-MWNTs (Figure 3b) for the same concentration. As the shear rate increased, the viscosity dropped initially in both cases. Shear thinning becomes prominent with increasing nanotube concentrations and larger tube aspect ratios (i.e., L-MWNTs). The slope of the shear-thinning region changed from $\approx -0.44$ to $-0.92$ as the MF of S-MWNT rose from 0.002 to 0.02.

For S-MWNT suspensions (Figure 3a), initial shear thinning was followed by a small extent of shear thickening. This viscosity rise was clearly observed at low nanotube MFs, whereas the viscosity increase was not significant for the highest S-MWNT MF. The degree of shear thickening was reduced by longer nanotubes (Figure 3b). L-MWNT samples did not display significant shear thickening. A small viscosity rise was only observed at $\approx 0.002$ MF (Figure 3b). Moreover, the increased viscosity could only be captured until the samples are ejected from the geometry causing a drastic viscosity drop (see dotted lines).

Figure 3c,d displays the dynamic rheological responses of silica suspensions in PEG-containing S-MWNTs and L-MWNTs, respectively. Silica in PEG without nanotubes exhibited a liquidlike behavior with $G'' > G'$. Both $G'$ and $G''$ increased with MWNT addition to silica suspensions. The dynamic moduli ($G'$, $G''$) are lower for fumed silica/MWNT/
PEG suspensions than for MWNT/PEG suspensions. The difference between $G'$ and $G''$ decreased in the LVE region, and ultimately $G' > G''$. For a given MWNT MF, the moduli decreased beyond a critical strain and a crossover between $G'$ and $G''$ occurred similar to MWNT-containing silica suspensions. This was particularly true for the samples containing L-MWNTs with fumed silica, at the highest MF. This decrease can be due to the disruption of the temporary network formation in nanotube suspensions.

Steady and dynamic rheological experiments on GONP suspensions with silica were performed to further analyze the effect of particle shapes on rheological behavior. Figure 4a displays the viscosity increase with addition of GONPs. For a given shear rate, the viscosity increased with the increasing amount of GONPs. The increase in viscosity is most pronounced at the GONP MF of 0.02, where the viscosity was about 1 order of magnitude greater than that for the fumed silica suspension at a 0.2 s$^{-1}$ shear rate. The GONP suspensions initially shear-thinned, prior to shear thickening. Adding GONP MFs of 0.01 and 0.02 decreased the critical shear rates of the fumed silica suspension from 80 s$^{-1}$ to 30 and 20 s$^{-1}$, respectively. Both $G'$ and $G''$ values increased with increasing GONP concentration (Figure 4b). $G'$ and $G''$ became similar in the LVE region for a 0.02 GONP MF, indicating viscoelastic fluidlike behavior. In contrast, $G'$ was higher than $G''$ for samples with nanotubes added to 0.15 MF fumed silica (Figure 3c).

The fumed silica suspension’s shear-thickening process can be explained by considering the formation of shear-induced hydroclusters. MWNTs or GONPs in fumed silica suspensions influence rheological responses and hydrocluster formation. Nanotubes disentangle and start to orient in the flow direction with increasing shear rates.50,58,59 The nanotube orientation in these suspensions depends on the flow strength, the large persistence lengths of nanotubes,61 and nanotube concentrations because their motion can be hindered in a crowded environment consisting of fumed silica and nanotubes. During nanotube orientational changes, portions of one nanotube can come into proximity with another nanotube. However, it is unlikely that multiple nanotubes will occupy close orbits forming hydroclusters. The PEG solvation layer also deters nanotube flocculations, as seen in some previous nanotube suspension studies, where shear thickening caused by flocculation was observed.32 Additionally, nanotubes can hinder hydrocluster formation by fumed silica particles themselves. Thus, shear thickening became less pronounced with increasing
nanotube concentration. A possible structural change during this process is shown in Figure 5a,b. Suspensions of GONPs with fumed silica shear-thicken. The GONPs are platelike particles with lateral dimensions similar to S-MWNTs but smaller than L-MWNTs. Unlike nanotubes, nanoplatelets cannot entangle, as manifested by their mostly viscoelastic fluidlike behavior, captured in their dynamic rheology (Figure 4b). The GONPs’ large surface area causes orientation in the flow direction trapping fumed silica particles between the platelets (Figure 5c,d). This can promote hydrocluster formation beyond \( \dot{\gamma}_c \). Thus, shear thickening was observed for these suspensions at lower \( \dot{\gamma}_c \).

The flow-history effect on sample microstructure and shear-thickening responses were analyzed by performing a sequence of rheology tests on 0.01 MF S-MWNT with 0.15 MF fumed silica samples. Strain sweep, flow sweep, and time sweep results appear in Figure 6. Strain sweep was initially conducted (step #1), showing \( G' > G'' \) in the LVE region, indicating a soft solidlike behavior. After conditioning (step #2), flow sweep (step #3) and strain sweep (step #4) were conducted. Interestingly, strain sweep (step #4) displayed a liquidlike behavior, as evident from \( G'' > G' \), indicating the structure changed during the flow sweep. The nanotubes may have disentangled (resulting in a drop of \( G' \)) and oriented during flow sweep. This sample was then relaxed for about 60 min, and increases in \( G' \) and \( G'' \) during relaxation were captured using a time sweep (step #5) where, \( G'' \) is still greater than \( G' \). Strain sweep (step #6) was performed after relaxation, causing a

Figure 6. Rheological test sequence for 0.01 MF of S-MWNT in a 0.15 MF fumed silica suspension. (a) Elastic and loss modulus vs strain amplitude, (b) viscosity vs shear rate, and (c) elastic and loss moduli vs time. The lines are for visual guidance. For clarity, every fourth data point is shown (complete data set is plotted in Figure S13).

Figure 7. Steady shear and dynamic rheology results for suspensions containing S-MWNT and fumed silica. (a) Steady shear viscosity vs shear rate, (b) elastic (\( G' \)) and loss (\( G'' \)) as a function of strain amplitude. The lines are for visual guidance. For clarity, every fourth data point is shown (complete data set is plotted in Figure S14).
viscoelastic liquidlike behavior and a smaller gap between $G'$ and $G''$. Time sweep (step #7) was conducted to allow further relaxation. Finally, shear thickening was captured next during flow sweep (step #8). These results (step #8) are different from those in first flow sweep (Figure S8). The nanotubes possibly lose their orientational order and start to entangle again during relaxation. Although a plateau was observed in the relaxation experiments, the structure did not fully recover its initial structure. A similar experiment was performed on only 0.15 MF fumed silica in PEG (Figure S9). We also compared the extent of shear thickening with step #8. The change in viscosity captured after the relaxation time exhibited a similar extent of shear thickening (Figure S10). However, the shear thickening in the nanotube-containing suspension is less pronounced than the one observed in fumed silica suspension (Figure S8).

The above results indicate that subjected shear flow, the entangled network-like structure is broken and nanotubes may have a flow-oriented structure. However, the shear-thickening process is mostly dictated by the fumed silica. To understand the effect of fumed silica on suspension rheological properties, flow sweep and strain sweep experiments were run on a constant S-MWNT MF of 0.01 and on two additional fumed silica MFs of 0.075 and 0.225. As the fumed silica MF rises from 0.075 to 0.225, the viscosity increased (~1 order of magnitude) over the whole shear-rate range (Figure 7a). Adding S-MWNTs had a larger effect on the low shear viscosity increase. For example, for the shear rate of 0.1 s$^{-1}$, the viscosity for a 0.075 MF of fumed silica is around 0.4 Pa s. This increased to about 100 Pa s upon adding a 0.01 MF S-MWNT. A steeper shear thinning and a greater extent of shear thickening were observed at the higher fumed silica MF of 0.225. However, the addition of S-MWNT hindered the shear-thickening process. This confirmed that S-MWNTs restrained shear thickening and hydrocluster growth even at higher fumed silica content. Strain sweep experiments on fumed silica suspensions (Figure 7b) displayed $G''$ higher than $G'$, indicating liquidlike behavior. $G'$ became greater than $G''$ upon adding S-MWNTs. The elastic moduli of fumed silica suspensions with S-MWNTs did not change significantly by raising the fumed silica MF from 0.15 to 0.225. However, a slight increase in $G''$ occurred with higher fumed silica contents, confirming that fumed silica did not play a crucial role in system elasticity.

Incorporation of anisotropic particles with high aspect ratios in fumed silica suspensions allows precise control of viscosity under shear. It is important to assess whether adding nanoparticles is beneficial in obtaining a similar behavior with lowering solid content. The 0.225 MF fumed silica suspension results here were compared with a suspension containing a 0.15 MF fumed silica and 0.02 MF GONP (Figure 8). A higher initial shear viscosity was observed upon addition of 0.02 GONP MF to 0.15 MF fumed silica in comparison to only 0.225 MF fumed silica in PEG. As the shear rate increased, the viscosity dropped for both samples. GONP addition decreased the critical shear rate from 100 to 10 s$^{-1}$ compared to the suspension with 0.225 MF fumed silica. This signifies the important effect of GONPs in the preparation of lightweight shear-thickening fluids. However, the GONP concentration may not be increased without limits because gel formation can occur at higher concentrations, as reported for GONP suspensions in water.42

Although GONP addition caused shear thickening, the addition of nanotubes did not induce this effect. We believe that MWNTs with higher flexibilities form entangled structures and prevent hydrocluster growth subjected to shear flow. Shear thickening can be enhanced by using shorter tubes without entanglements. It is also worth exploring the incorporation of stiffer tubes to tune the dynamic and steady flow behavior of fumed silica suspensions. We also anticipate that our results will be valid for any suspensions, including mixed-particle suspensions, where the suspended particles can form hydrogen bonding with the suspending media. In addition, we speculate that nanotubes suspended with the aid of surfactants in nonpolar solvents will also show shear-thickening behavior.

**CONCLUSIONS**

In this study, the effect of surface-functionalized MWNTs and GONPs on the rheological behavior of fumed silica suspensions was investigated. The functional groups on these particles form hydrogen bond with PEG, resulting in stable suspensions. Addition of MWNTs and GONPs in fumed silica suspensions increased the viscosity and elastic moduli of the suspensions. For the MWNT suspensions, the elastic modulus was found to be higher than the loss modulus at low strain, i.e., the samples behave like soft solids. Such elastic behavior is attributed to the entangled network structure of nanotubes. Fumed silica suspensions when subjected to shear flow display a shear-thickening behavior beyond a critical shear rate. However, for the nanotube suspensions, the shear-thickening behavior disappeared with increasing concentration of nanotubes, likely because of difficulty in forming hydroclusters. In contrast, GONPs enhance the shear-thickening behavior. Adding only a 0.02 MF GONP into a 0.15 MF fumed silica decreased the critical shear rate from 100 to 10 s$^{-1}$ in comparison to a 0.225 MF fumed silica suspension. The GONPs’ large surface area causes trapping of fumed silica particles between the platelets and the formation of hydroclusters. Our results indicate that the rheological behavior of dense, mixed-particle suspensions can be tailored by changing the concentration and the aspect ratios of the suspended particles.

**MATERIALS AND METHODS**

Aerosil 200 silica or A200 (Evonik Industries), two types of MWNTs (Cheap Tube Inc.) with different lengths, 0.5–2 and 10–30 μm, respectively, but of the same diameter (outer diameter, 10–20 nm) were used. These tubes are defined as short MWNTs (S-MWNTs) and long MWNTs (L-MWNTs), respectively. GONPs were synthesized using exfoliated graphite provided by Asbury Carbons (CAS #7782-42-5, grade 3806).

**Figure 8.** Viscosity vs shear rate for 0.225 MF of fumed silica in PEG, and 0.02 MF GONPs in 0.15 MF fumed silica in PEG. For clarity, every third data point is shown (complete data set is plotted in Figure S15).
An improved Hummers’ method was used for GONP synthesis. Hydroxy-terminated poly(ethylene glycol) (PEG), with an average molecular weight of 200 (PEG 200), was purchased from Fisher Scientific and used as received.

Characterization. Transmission electron microscopy (TEM) and atomic force microscopy (AFM) were utilized to characterize the nanoparticles. A JEOL 2100 200 kV microscope captured the TEM images. Dilute GONPs in water were deposited on 300 mesh formvar lacy carbon-coated copper grids for TEM experiments. TEM was also used to study the suspensions consisting of fumed silica only and fumed silica and MWNTs/GONPs suspended in PEG 200. Here, the suspension of interest was diluted with ethanol, deposited on carbon-coated copper grids. Ethanol was removed under vacuum for 2 h before TEM experiments. A Dimension Icon atomic force microscope (Bruker Corporation) was used for AFM imaging. A drop of a dilute GONP water solution was deposited on a glass substrate and dried before each AFM experiment. A silicon nitride probe with a spring constant of 3 N/m was used.

X-ray diffraction (XRD) experiments were conducted using a Cu Kα1 radiation (λ = 1.5406 Å) in the 2θ range of 5–50°. The GONPs’ degree of oxidation was characterized using a K-α X-ray photoelectron spectrometer (Thermo Fisher Scientific) with an Al Kα (1486.6 eV) X-ray source. The survey and high-resolution (HR) spectra were taken at pass energies of 200 and 40 eV.

Fourier transform infrared (FTIR) spectrometry experiments were conducted using a Nicolet 6700 FTIR spectrometer (Thermo Scientific Co.). All experiments were conducted in transmission mode, and each spectrum was captured from 600 to 4000 cm⁻¹ by averaging 32 scans at a resolution of 4 cm⁻¹.

Sample Preparation. Initially, nanotube/PEG samples were sonicated using a tip sonicator (Fisher Scientific, CL-334) at 80 W for 15 min. A200 silica was then mixed into that suspension using a high-shear mixer (Silverson L4RT-A) at 6000 rpm for 40 min, giving homogeneous suspensions. Air bubbles were removed by vacuum degassing for 12 h. Samples with GONPs were prepared by this same procedure, except that a bath sonicator (Branson CPX1800H) was used for 4 h instead of the tip sonicator. All samples had a 0.15 MF of A200 silica if not indicated otherwise. The MFs of MWNTs, GONPs, and PEG were calculated by considering constant total mass. The true densities of A200 silica, MWNT, and GONP were 2.22, 2.1, and 2.26 g/mL, respectively.

Rheological Experiments. Steady and dynamic shear rheology experiments were performed using a TA Instruments Discovery Hybrid 2 rheometer with 40 mm parallel plates at 20 °C. The gap was maintained at 1 mm. Strain sweep experiments were performed by varying the strain amplitude from 0.1 to 1000% at a frequency of 1 rad/s. Flow sweep experiments were performed at the shear rates of 0.1–1000 s⁻¹. A 60 s prestrain step at a shear rate of 1 s⁻¹ was applied before the flow sweep tests. All experiments were repeated at least three times on two different sample batches (six total repeats). The error bars on the rheological results indicate one standard deviation. For the same batch, the experimental variation was very small, but the variation was as high as 20% between two different batches.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01484.

Characterization of nanoparticles using TEM, AFM, XRD, and XPS techniques and fumed silica/nanoparticle suspension characterizations by FTIR and rheology (PDF)

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Notes

The authors declare no competing financial interest.

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