Rheology of concentrated carbon nanotube suspensions

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The rheological properties of non-Brownian carbon nanotube suspensions are measured over a range of nanotube volume fractions spanning the transition from semidilute to concentrated. The polymer-stabilized nanotubes are “sticky” and form a quiescent elastic network with a well-defined shear modulus and yield stress that both depend strongly on nanotube volume fraction with different but related critical exponents. We compare controlled-strain-rate and controlled-stress measurements of yielding in shear flow, and we study the effect of slow periodic stress reversal on yielding and the arrest of flow. Our measurements support a universal scaling of both the linear viscoelastic and steady-shear viscometric response. The former allows us to extract the elastic shear modulus of semidilute nanotube networks for values that are near or below the resolution limit of the rheometers used, while the latter provides a similar extrapolation of the yield stress. A simple scaling argument is used to model the dependence of yield stress and elastic modulus on concentration. © 2007 American Institute of Physics. [DOI: 10.1063/1.2711176]

I. INTRODUCTION

Carbon nanotubes exhibit remarkable physical properties and there is currently a great deal of interest in using them in a new generation of materials and applications. Despite this promise and potential, carbon nanotube melts and suspensions are inherently difficult to process, even in just the semidilute regime, and efficient processing schemes are only just starting to be formulated. The large aspect ratios and attractive inter-particle interaction potentials inherent to carbon nanotubes can give rise to undesirable effects—such as mechanical entanglement and flow-induced clustering—when carbon nanotube suspensions and melt-composite materials are subjected to an external shear stress, which in turn puts limits on the efficient flow processing of such materials. In light of these issues, it would be beneficial to know the generic response of non-Brownian viscoelastic carbon-nanotube suspensions to changes in some of the key variables that control and limit flow processing, such as nanotube composition, the magnitude of the applied shear stress, and flow rate.

The shear rheology of carbon nanotube suspensions is a relatively young field of research. Previous work has focused on the viscometric response of single-wall carbon nanotubes dispersed in both water and super-acid solvents, focusing in particular on the relationship between the intrinsic shear viscosity and mean carbon nanotube length. Additionally, a number of groups have used oscillatory shear flow as a tool to quantify the interplay between carbon nanotube percolation and linear viscoelasticity. In concentrated aqueous suspensions of single wall carbon nanotubes, insightful analogies have been drawn with biological filamentous networks such as those composed of actin. Linear viscoelasticity in composite polymer carbon nanotube melts has similarly been interpreted in terms of a diffuse network structure. The oscillatory and steady-shear response of melt polymer composites containing predominantly multiwalled carbon nanotubes—a topic of particular relevance to the efficient flow processing of electrically conductive plastics—has also been investigated by several groups. Huang et al. have established working relationships between mixing time and network elasticity for polymer composites containing aggregates of nanotube bundles, while some of the connections between melt rheology and electrical conductivity in percolated carbon nanotube networks have also been studied in detail. A very practical and important problem that has received considerable recent attention is the establishment of flow-structure and structure-property relationships with relevance to the melt processing of carbon nanotube polymer composites, focusing in particular on the issue of nanotube dispersion. For concentrated suspensions, some questions as to the nature and extent of carbon nanotube solubility and exfoliation remain unaddressed, while some aspects of the interplay between polymer melt viscoelasticity and the rheological properties of carbon nanotube networks remain poorly understood. Low-viscosity Newtonian polymer solvents would be particularly useful in this regard, as they can impart significant shear stress to hierarchical nanotube structures without masking their viscoelastic response.

In this paper we report an experimental study of the rheological properties of non-Brownian carbon nanotube suspensions over a range of nanotube concentrations spanning the transition from the semidilute to concentrated regimes. Although coated with a polymeric dispersant, the carbon nanotubes are inherently sticky and form a quiescent elastic network with a well-defined shear modulus and yield stress, both of which depend strongly on a nanotube concentration with distinct but related power-law exponents. The viscosity of the polymeric solvent is high enough to achieve ideal carbon nanotube dispersion under strong shear flow, but...
sufficiently low as to not mask the rheological response of the nanotube network. We compare controlled-strain-rate and controlled-stress measurements of yielding in steady shear flow, and we study the effect of cyclic stress reversal on shear thickening and the arrest of flow. Our measurements suggest a universal scaling of both the linear viscoelastic and steady-shear viscometric response. In turn, these scaling relations allow us to extrapolate both the elastic shear modulus and yield stress of the nanotube network at concentrations in the semidilute regime for which the magnitude of these quantities are near or below the resolution limits of the rheometers used in this study. The data are interpreted through a comparison of the steady shear and linear viscoelastic response, and a simple scaling argument is used to quantitatively link the concentration dependence of the yield stress and shear modulus of the nanotube network.

II. MATERIALS, METHODS, AND BACKGROUND

Multiwalled carbon nanotubes (MWNTs) were grown through chemical vapor deposition (CVD) and suspended in a low-molecular-mass polyisobutylene (PIB) fluid using a polysucinimide dispersant as described elsewhere.\textsuperscript{2,19} Electron microscopy gave a mean diameter of $d = 50$ nm and the mean contour length was determined optically to be $L = 10$ $\mu$m, with $L/d = 200$. For an isolated tube, the persistence length is comparable to or larger than $L$, while the size distribution is nearly log-normal with a polydispersity index of 2. We use a Newtonian PIB fluid with $M_w = 500$ and a shear viscosity, $\eta_s$, of $0.5$ Pa s. Suspensions were prepared at $0.025\%$ to $10\%$ MWNT by mass with $6 < c L^3 < 2500$ and $0.03 < c L^2 d < 13$, where $c$ is the number of nanotubes per unit volume, spanning the transition from the dilute to concentrated regimes for rigid rods\textsuperscript{20}. To convert from mass fraction to volume fraction, we assume a mass density that is comparable to graphite (approximately $2$ g/cm$^3$) for the MWNTs of interest here, which are relatively large by carbon nanotube standards. The concentration that approximately delineates dilute from semidilute is $c L^3 \approx 1$, or $0.005\%$ MWNT by mass. The nanotubes have an attractive interparticle potential on the order of several $k_BT$ and flocculate in quiescence, but they can be fully dispersed with shear flow in the viscous PIB solvent of interest here.\textsuperscript{2}

We consider linear shear flow along $\hat{x}$ with a constant velocity gradient along $\hat{y}$ and vorticity along $\hat{z}$. The strain rate is $\dot{\gamma} = \partial u / \partial y$ and all measurements reported here were performed at $25$ $\degree$C. To minimize melt hysteresis, the MWNT suspensions were first homogenized at high shear rate and then subjected to a temporally decaying large-amplitude oscillatory shear flow prior to measurement. Video microscopy measurements of the sheared suspensions were also performed in a parallel-plate controlled-strain optical shear cell\textsuperscript{21} with a variable gap, $h$. The shear stress ($\sigma = \sigma_{yy}$), the steady shear viscosity ($\eta_s$), the first normal stress difference ($N_1 = \sigma_{xx} - \sigma_{yy}$), where $\sigma_{ij}$ is the stress tensor), and the complex shear modulus, $G'(\omega) = G''(\omega) + iG'''(\omega)$, were measured independently in a controlled-strain cone-and-plate rheometer. A controlled-stress rheometer was used in both cone-and-plate and parallel-plate geometries to measure $\eta(\gamma)$, where $\gamma$ is the cumulative strain in response to an applied external shear stress. Measurements in cone-and-plate geometry were performed using both $25$ and $50$ mm plates with a center gap appropriate to the specified cone-angle as designated by the manufacturer to ensure a homogeneous strain rate throughout the sample. Measurements in parallel-plate geometry were performed with both $25$ and $50$ mm plates at different gaps, which typically varied between $0.5$ and $1$ mm.

The geometry of shear flow is shown in Fig. 1. Due to their strong optical absorption and macroscopic length, individual MWNTs can be observed under shear with stroboscopic video microscopy. The apparent diameter in such images reflects the quality of the optics used to image the nanotubes and is not a robust measure of the MWNT diameter. The sheared nanotubes are in periodic Jeffery orbits around $\hat{z}$ with interactions dictating the distribution of such orbits (and hence the orientational distribution function) in the semidilute regime.\textsuperscript{22} In semidilute suspensions at sufficiently small $h$, we can directly observe these orbits as the MWNTs pass through the field of view. Longer nanotubes were observed to spend the majority of their orbit aligned with streamlines along the flow direction, with a “flipping” event mid-cycle. As viewed in the $x$-$z$ plane, these projected rotations appear to occur in either the $x$-$z$ or $x$-$y$ planes. We also observed “contact” interactions between neighboring trajectories in which a flipping nanotube collided with another, altering the nature of both orbits. In contrast, shorter MWNTs tended to reside in orbits in which they appeared to rock back and forth around the vorticity direction. In concentrated suspensions, contact interactions undoubtedly become increasingly important as the MWNT concentration, $\phi$, increases. Based on these observations, we anticipate that much of the rich literature on the rheology of non-Brownian fiber suspensions\textsuperscript{22} should be relevant and applicable to the carbon nanotube suspensions of interest here.

The deformation of comparable MWNTs has been measured.\textsuperscript{23} The Young’s modulus ($E_Y \approx 40$ GPa) and bending stiffness ($B = E_Y \pi d^4 / 2 \approx 1.22 \times 10^{-20}$ nm$^2$) compare with $7.5$ MPa and $8 \times 10^{-12}$ nm$^2$, respectively, for typical organic fibers.\textsuperscript{24} Modeling the suspended MWNTs as extended fibers, the dimensionless bending stiffness, $B/(\eta_s \gamma d L^4)$, and bending ratio, $E_Y [\ln(2\gamma r_e)]^{-1.5} d^3 / (2\eta_s \gamma d L^4)$ where $r_e = 1.24 (L/d) [(\ln(L/d))^3/2]$, are $0.02$ and $0.5$, respectively, at $100$ s$^{-1}$. For dimensionless bending ratios less than $1$, isolated fibers will deform in response to the viscous shear stress in the solvent.\textsuperscript{24,25} In concentrated suspensions, however, recent simulations have highlighted the important and interrelated roles of inter-fiber friction, fiber shape, and fiber
bending, and particle interactions in such suspensions will likely promote nanotube deformation at shear rates below those cited above for isolated nanotubes.

At the smallest $\dot{\gamma}$, the bare rotational Peclet number, $\text{Pe} = \pi \eta L^3 \dot{\gamma} / 3k_B T \ln(L/d) - 0.8$, is larger than one, and the MWNT suspensions are non-Brownian. The Reynolds number, $\text{Re} = \dot{\gamma} h^2 \rho / \eta$, where $\rho$ is the solvent mass density, is always much less than 1, while the Weissenberg number, $Wi = N_1 / \sigma$, is typically larger than 1 in magnitude, implying that elastic effects are important while inertial effects can be neglected. In dilute suspensions, isolated MWNTs are observed to slowly sediment under the action of gravity over the course of several days. In the semidilute and concentrated suspensions of interest here, however, we found that the MWNTs tended to form stable self-supporting networks. Although isolated MWNT aggregates can also sediment out of suspension, such objects likewise formed diffuse macroscopic self-supporting structures spanning the gap of the flow cell in the suspensions of interest here. Since the samples were all subjected to a rigorous preshear treatment in the suspensions of interest here, however, we found that the MWNTs tended to form stable self-supporting networks. Despite being coated with a polymer dispersant, the MWNT suspensions are non-Brownian. The clustering has a distinct rheological signature, however, that can be used in a limited range of concentration (below 10%) to assess the state of dispersion. The growth of isolated macroscopic clusters suspended in PIB leads to a temporal increase in the steady shear viscosity as measured in a step-rate experiment, as shown in Fig. 3. At later times, a more gradual decrease in viscosity has been linked to the compressibility of clusters and $N_1 < 0$ in semidilute suspensions. The appearance of a well-defined peak in the time evolution of the shear viscosity after a step-rate quench can thus be taken as a reasonable indication of MWNT flocculation. Figure 3 shows $\eta(t)$ at 0.1 s$^{-1}$ (cone-and-plate geometry in controlled strain mode) for three different $\phi$. While both 1.7% and 3% show viscous enhancement reflecting the breakup of the global network and the subsequent growth of clusters, 6% shows little change, suggesting that a network structure remains somewhat intact at high nanotube concentrations and low shear rates when subjected to a controlled strain-rate experiment.

III. RESULTS AND DISCUSSION

Steady and oscillatory controlled-strain rheology data for the suspensions are shown in Figs. 4 and 5. For lack of a better point of reference, the shear stress in Fig. 4 and the steady shear viscosity in Fig. 5(a) both correspond to the maximum in $\eta(t)$ following a step-rate quench of the type shown in Fig. 3. Oscillatory measurements in Fig. 5(b) were taken at a strain amplitude in the regime of linear response, which decreases monotonically from 0.02 with increasing $\phi$. Samples at high $\phi$ exhibit order-of-magnitude viscosity enhancement coupled with dramatic shear thinning, as shown in Fig. 5(a). This is mirrored by the emergence of a well-defined plateau in $G'(\omega)$, indicative of a “solidlike” linear
viscoelastic response at low \( \omega \). In the semidilute regime, the transient rheology of cluster formation suggests that \( N_1 \) becomes modestly negative at late times.\(^2\) At 10\% MWNT by mass, which is well into the concentrated regime, the average \( N_1 \) measured in a step rate test varied from around \(-600 \) Pa at \(0.07 \) s\(^{-1}\) to around \(500 \) Pa at \(20 \) s\(^{-1}\). There was a considerable variation from run to run, however, and \( N_1 \) was extremely sensitive to the sample preshear history. Large negative \( N_1 \) were only observed if the network elasticity evident in Fig. 5(b) was allowed to recover after preshearing before steady shear was applied.

As recently reported for particle gels\(^28\) and 2D colloidal monolayers,\(^29\) a universal scaling plot can be constructed from the oscillatory-shear data in Fig. 5(b), as shown in Fig. 6. Although physically there can only be one linear-viscoelastic shear modulus, \( \kappa(\phi) \), there is a degree of relative uncertainty in the comparative measurement of loss and storage at varied \( \phi \) and \( \omega \) in Fig. 5(b), and the approach we adopt here is to scale each part of this response separately, demonstrating after the fact that \( \kappa(\phi) \) and \( \kappa(\phi) \) are indistinguishable within experimental resolution. As such, two distinct parameters, \( \kappa(\phi) \) and \( \kappa(\phi) \), are initially used to reduce \( G'(\omega) \) and \( G''(\omega) \), respectively, in Fig. 5(b), with the relaxation time \( \tau(\phi) \) used to reduce the horizontal axis being \( \eta_0/\kappa(\phi) \) for \( G'(\omega) \) and \( \eta_0/\kappa(\phi) \) for \( G''(\omega) \). We choose \( \eta_0 = 2 \) Pa s (equal to \( 4 \) \( \eta_0 \)) to render the horizontal scale dimensionless as this makes the two response curves in Fig. 6 coincide at \( \omega \tau = 1 \). As shown below in Fig. 8 and as expected physically, there is no significant difference between \( \kappa(\phi) \) and \( \kappa(\phi) \), with the data suggesting that both scale as \( d^\alpha \) with \( \alpha = 7.1 \pm 0.3 \). In the high-frequency limit, the data suggest \( G'/\kappa \propto (\omega \tau)^{0.7} \) and \( G''/\kappa \propto (\omega \tau)^{0.9} \). We note that both the shape of the scaling curve and the high-\( \omega \) power-laws are qualitatively similar to those predicted for semiflexible polymer networks,\(^30\) although the \( \phi \) dependence of the modulus that we infer from this scaling plot (Fig. 8, discussed in detail below) is much stronger. It is also important to emphasize that the \( \phi \) dependent scaling parameter shifts both the vertical and horizontal scales in Fig. 5(b), and it is thus not strictly correct to obtain \( \kappa(\phi) \) by simply reading off a \( \phi \)-dependent modulus at a fixed low frequency. From a scaling curve of the type shown in Fig. 6 we are, in effect, inferring elastic moduli for semi-dilute MWNT networks that are quite “soft,” with values at or below the resolution limit of the rheometers.

To scale the steady-shear viscometric response shown in Figs. 5(a) in a similar fashion, we divide both stress and shear rate in Fig. 4 by the \( \phi \)-dependent stress \( \sigma_0(\phi) \) to get the scaling plot in Fig. 7. This scaling plot is motivated by the simple Bingham model of a yield stress fluid, which identifies \( \sigma_0(\phi) \) as a yield stress. To make the horizontal axis dimensionless, we have multiplied \( \dot{\gamma}/\sigma_0(\phi) \) by the solvent viscosity, \( \eta_0 \). The data fall into two distinct power-law regimes that delineate semidilute (with a power-law exponent of 0.7) from concentrated (with a power-law exponent of 1/3). In the same manner that we extracted the network shear modulus from the scaling plot in Fig. 6, we thus extrapolate the network yield stress, \( \sigma_0(\phi) \), from the scaling plot in Fig. 7. The \( \phi \) dependence of \( \sigma_0 \), also shown in Fig. 8,
is significantly weaker than that of $\kappa$, with $\sigma_0 \propto \phi^{3.5}$. Comparable exponents for the dependence of yield stress on concentration have been measured and modeled for fiber suspensions,\textsuperscript{26} where this exponent typically varies between 2.5 and 3.5.

The observations made in both steady and oscillatory controlled-strain measurements described above portray an elastic carbon nanotube network that yields under sufficient stress. Not surprisingly, this leads to intriguing yield-stress behavior that can be directly assessed with a controlled-stress rheometer. Stress-controlled cone-and-plate measurements of $\eta(\gamma)$ as a function of $\sigma$ at 6 % MWNT by mass are shown in Fig. 9(a). Below $\sigma_{\text{c}} \approx 40$ Pa, the system flows for a measurable strain as the viscosity increases and the flow starts to arrest, while above $\sigma_{\text{c}}$ the suspension flows indefinitely. The $\phi$ dependence of the yield stress $\sigma_{\text{c}}$ is shown in Fig. 8 along with that of $\kappa$ and $\sigma_0$. Again, we find a weaker $\phi$ dependence for $\sigma_{\text{c}}$ than that observed for $\kappa$, with $\sigma_{\text{c}}(\phi)$ being comparable to $\sigma_0(\phi)$, suggesting that the two methods of measuring yield stress are equivalent.

Similar to what has been demonstrated in concentrated suspensions of non-Brownian spheres by Knipmeyer and Pine,\textsuperscript{31} the response of the carbon nanotube melts to a slow square-wave stress is intriguing. The response of a 3 % MWNT suspension to a slow square-wave stress of amplitude 10 Pa in a cone-and-plate geometry is shown in Fig. 9(b). Such “work hardening” likely arises from small reconfigurations in the structure of the MWNT network that strengthen it against shear deformation. The response of a 6% suspension to a slow square-wave stress of amplitude 10 Pa in a parallel-plate geometry is shown in Fig. 9(c). The suspension initially “jams” in both directions, but then starts to flow. Although $\sigma$ is below $\sigma_{\text{c}}$ at this $\phi$, the strain rate is not constant throughout the gap, and the material thus yields at lower stress, which we attribute to a breakup of the outer load-bearing portion of the network. Controlled-stress optical measurements at 3 % MWNT are inconclusive regarding detailed changes in network structure when the suspensions are quenched below $\sigma_{\text{c}}$, although intuitively one would just expect the network to show microscopic rearrangements to accommodate the load.

The different critical exponents suggested by the yield stress and the elastic modulus are interesting and intriguing. An intuitive explanation is that the number of physical tube-tube contacts, or “bonds,” associated with yielding is less than that associated with small-deformation linear viscoelasticity. Equivalently, one might suggest that there are a minimal number of critical bonds or “links” that survive in the strained network, which in turn serve to resist yielding and flow. Using the same physical arguments that we previously used to relate $\kappa$ to the morphology of the MWNT network,\textsuperscript{52} we can quantitatively account for the smaller critical exponent exhibited by the yield stress. A simple scaling model of fractal gels in three dimensions gives $\alpha = (3 + D_f)/(3 - D_b)$, where $D_f$ and $D_b$ are the network and backbone fractal dimension, respectively.\textsuperscript{33} The exponent $D_f$ describes the diffuse nature of the nanotube network, with $N(r)$ — the number of nanotube mass elements contained within a sphere of ra-
which grow with nanotube volume fraction in a power-law fashion with markedly different critical exponents that can be related to each other through a simple scaling argument. Controlled-strain and controlled-stress measurements of yielding in steady shear flow give comparable values of yield stress, and we show that slow periodic stress reversal leads to subtle changes in network properties akin to either strain hardening or strain softening, depending on the geometry of the flow. Scaling of \( G'(\omega) \) allows us to extrapolate the elastic shear modulus of semidilute nanotube networks at values that are near or below the resolution limit of the rheometers used in this study, while scaling of steady-shear viscometric data for \( \sigma(\dot{\gamma}) \) provides a similar low-\( \dot{\gamma} \) extrapolation of the yield stress. Our measurements highlight the quantitative link between the viscometric and linear-viscoelastic response functions.

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