Modeling elastic behaviour in functionalized carbon nanotube suspensions

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ABSTRACT: This work reports recent experimental findings and rheological modeling on chemically treated single-walled carbon nanotubes (CNTs) suspended in an epoxy resin. When a CNT suspension is subject to a steady shear flow, it exhibited a shear-thinning characteristic, which was subsequently modeled by a Fokker-Planck (FP) simple orientation model. In terms of viscoelasticity, small-amplitude oscillatory measurements revealed mild elasticity for semi-dilute CNT suspensions. Some tentative models are proposed in order to model the extra contribution of elasticity due to the presence of CNTs.

Key words: Carbon nanotubes, Brownian dynamics simulation, Viscoelastic behaviour

1 INTRODUCTION

This work reports recent experimental findings and rheological modeling on chemically treated single-walled carbon nanotubes (CNTs) suspended in an epoxy resin. When a CNT suspension is subject to a steady shear flow, it exhibits a shear-thinning characteristic. In terms of viscoelasticity, small-amplitude oscillatory measurements revealed mild elasticity for semi-dilute CNT suspensions. A "quasi-network" model was proposed in order to model the extra contribution of elasticity due to the presence of CNTs. The model postulates that for a treated CNT suspension at rest, there exists an equilibrium orientation distribution of CNTs and given the mutual repulsive force between treated CNTs, an isotropic orientation distribution is expected to be the most energy favorable configuration. It is conjectured that CNTs interact via repulsive force but there is no physical contact between them in a semi-dilute suspension. Small-amplitude oscillations perturb this orientation distribution, with a tendency for the CNTs to return to an isotropic orientation distribution. The network model predicts that both G" and G' increase as a function of frequency. This paper revisits the main orientation mechanisms that allow defining a large variety of mechanical models.

2 MECHANICAL MODELING

2.1 Nanotube kinematics

In what follows the carbon nanotubes are modeled as rigid rods suspended in a Newtonian matrix whose kinematics is assumed undisturbed by the nanotubes presence. A simple rheological flow is supposed taking place. From the dynamical point of view these rods consist of two beads (in which the fluid effects are localized) connected by a rigid rod that only serves to connect both beads.

The fiber center of gravity is assumed translating with the flow. Thus, fixing the origin of the coordinates system on the fiber center of gravity the location of the tube beads is given by:

$$\mathbf{x}_b = \pm L\mathbf{p} \qquad (1)$$

where L is the tube half length and $\mathbf{p}$ is an unitary vector aligned with the fiber direction. In what follows we focus our analysis in one of the tube beads. We assume that at the tube scale the gradient of the velocity field remains constant.

Different forces are acting on the tube:

➢ Flow drag. This force is proportional to the difference of velocities existing at each bead between the undisturbed fluid velocity $\mathbf{v}_f$ and the bead velocity $\mathbf{v}_b$, that is:

$$\mathbf{F}_{drag} = \zeta\left(\mathbf{v}_f - \mathbf{v}_b\right) = \zeta L\left(\nabla\mathbf{v}\cdot\mathbf{p} - \dot{\mathbf{p}}\right) \quad (2)$$

being its associated torque:

$$\mathbf{T}_{drag} = 2L\mathbf{p}\times\mathbf{F}_{drag} \quad (3)$$

where "$\times$" denotes the vector product and the existence of two beads has been taken into account. It can be noticed that the net force due to the drag forces is zero, because the forces acting on both beads have the same value but opposite directions.

➢ External torque. Tubes can be subjected to torques generated by external sources or even from the electrostatic interaction with all the surrounding tubes. These torques will be denoted by $\mathbf{T}_{ext}$.

➢ Inertia. The inertia effects associated with the tubes rotation could be retained in the model by considering

$$\mathbf{F}_{inert} = mL\ddot{\mathbf{p}} \quad (4)$$

being m the bead mass. Then the torque writes:

$$\mathbf{T}_{inert} = 2L\mathbf{p}\times\mathbf{F}_{inert} \quad (5)$$

➢ Brownian effects. The beads are subjected to mechanical interaction with other nanotubes beads as well as to the continuous bombardment coming from the solvent molecules thermally activated. These impacts are usually modeled using random forces acting on the beads. These random effects introduce a characteristic time and then an intrinsic elastic behavior. These effects will be addressed later but ignored by the moment.

Now, the equilibrium of torques (neglecting Brownian effects) implies:

$$\mathbf{T}_{drag} + \mathbf{T}_{ext} + \mathbf{T}_{inert} = \mathbf{0} \quad (6)$$

We are only addressing 2D models and two scenarios will be considered:

I. Only the drag effect acting on the tubes are retained in the model. In this case $\mathbf{T}_{ext} = \mathbf{0}$ and $\mathbf{T}_{inert} = \mathbf{0}$, and then Eqs. (6) and (3) lead to:

$$\dot{\mathbf{p}} = \nabla\mathbf{v}\cdot\mathbf{p} - \left(\mathbf{p}^T\cdot\mathbf{D}\cdot\mathbf{p}\right)\mathbf{p} = \nabla\mathbf{v}\cdot\mathbf{p} - \left(\mathbf{D}:\left(\mathbf{p}\otimes\mathbf{p}\right)\right)\mathbf{p} \quad (7)$$

where $\mathbf{D}$ is the strain rate tensor[1]. Eq. (7) coincides with the expression obtained by Jeffery in the particular case of fibers with an infinite aspect ratio. Now, assuming a 2D modeling, that allows writing $\mathbf{p}^T = (\cos\varphi, \sin\varphi)$, and assuming the simple shear flow defined by $\mathbf{v}^{\mathrm{T}} = \left(\dot{\gamma}y, 0\right)$, Eq. (7) writes: $\dot{\varphi}(\varphi) = -\dot{\gamma}\sin^2\left(\varphi\right)$. We can notice that the tubes rotate and tend to align along the flow direction $\left(\varphi = 0\right)$.

II. Drag and inertia effects coexist. In this case, with $\mathbf{T}_{ext} = \mathbf{0}$, Eqs. (6), (3) and (5) lead to:

$$\ddot{\varphi}(\varphi,\dot{\varphi}) = -\frac{\zeta}{m}\left(\dot{\varphi} + \dot{\gamma}\sin^2\left(\varphi\right)\right) \quad (8)$$

2.2 Computing stresses

Firstly, we consider the simplest scenario: a CNT dilute suspension with neither external torques nor inertia effects. Because of the dilute scenario, Brownian effects can be in first approximation also neglected. For the sake of simplicity we consider all the models defined in two-dimensions and the undisturbed simple shear flow previously introduced. In this case, the rotation velocity results from Eq. (7), leading to the drag force acting on each bead:

$$\mathbf{F}_{drag} = \zeta L\dot{\gamma}\sin\left(\varphi\right)\cos\left(\varphi\right)\begin{pmatrix}\cos\left(\varphi\right)\\ \sin\left(\varphi\right)\end{pmatrix} \quad (9)$$

or:

$$\mathbf{F}_{drag} = \zeta L\dot{\gamma}\sin\left(\varphi\right)\cos\left(\varphi\right)\mathbf{p} \quad (10)$$

that proves that the applied force is collinear with the tube. The virial stress for a population of N tubes (within an elementary volume) results:

$$\boldsymbol{\tau} = -\sum_{i=1}^{i=N} 2L\mathbf{F}_i^B\otimes\mathbf{p}_i \quad (11)$$

where $\mathbf{F}^B$ is the sum of the forces (except the viscous one) applied on the bead. In any case, as we are considering the force transmitted from the beads connector to each bead, the drag forces are implicitly taken into account. The connector tension can be

[1] "$\otimes$" denotes the tensor product $\left(\mathbf{a}\otimes\mathbf{b}\right)_{kl} = \left(\mathbf{a}\right)_k\left(\mathbf{b}\right)_l$, and ":" the tensor product twice contracted, i.e. $\left(\mathbf{a}:\mathbf{b}\right) = \sum_{k,l}\left(\mathbf{a}\right)_{kl}\left(\mathbf{b}\right)_{kl}$.

calculated by enforcing the bead equilibrium[2]. Thus, introducing Eq. (10) into Eq. (11) it results:

$$\boldsymbol{\tau} = \sum_{i=1}^{i=N} 2L^2 \zeta \dot{\gamma} \cos(\varphi_i) \sin(\varphi_i) \mathbf{p}_i \otimes \mathbf{p}_i \qquad (12)$$

proving the expected symmetry of the extra-stress tensor due to the presence of the CNTs and also proves that this extra-stress depends on the tubes concentration (number of fibers), tubes shape (length) as well as on their orientations. Tubes aligned in the flow direction or perpendicularly to this direction do not resist the flow leading to a null extra-stress. The maximum extra-stress is obtained when all the tubes align at $\pi/4$ with respect to the flow direction. It is easy to prove that in the general case the extra-stress tensor (12) writes:

$$\boldsymbol{\tau} = 2L^2 \zeta \sum_{i=1}^{i=N} \mathbf{D} : (\mathbf{p}_i \otimes \mathbf{p}_i \otimes \mathbf{p}_i \otimes \mathbf{p}_i) \qquad (13)$$

Obviously this expression is also valid for general flows and not only in the case of the simple shear flow here considered.

The procedure just described can be generalized to address more general situations involving different forces acting on the dumbbells. In what follows we are analyzing the effects of random forces and external torques in the simple shear 2D flow previously introduced:

- Introducing Brownian effects. We are analyzing the contribution of these effects on the extra-stress tensor. The first consequence, but not the only one, is that the presence of Brownian effects alters the orientation distribution involved in the expression (13). Moreover, the applied random forces will contribute to the extra-stress tensor. To evaluate this extra-contribution we start recalling that rotational Brownian effects could be interpreted as a kind of rotary diffusion (as it is usually modeled within the kinetic theory framework) producing a random rotation of mean equal to zero and a standard deviation equal to $\sqrt{2D_r \Delta t}$, that is: $\Delta\varphi_{rand} = \Re\left(0, \sqrt{2D_r \Delta t}\right)$, which could be associated with the random rotary velocity: $\Delta\varphi_{rand} = \dot{\varphi}_{rand} \Delta t$; from which it results:

$$\dot{\varphi}_{rand} = \frac{\Delta\varphi_{rand}}{\Delta t} = \frac{\Re\left(0, \sqrt{2D_r \Delta t}\right)}{\Delta t} = \Re\left(0, \sqrt{\frac{2D_r}{\Delta t}}\right) \qquad (14)$$

whose associated torque is:

$$\mathbf{T}_{rand} = 2LF_{rand} (\mathbf{p} \times \mathbf{t}) = \zeta_r \Re\left(0, \sqrt{\frac{2D_r}{\Delta t}}\right) \mathbf{e}_z \qquad (15)$$

where F_{rand} represents the component of the random force applied on the bead in the angular direction defined by the unit vector $\mathbf{t}^T = (-\sin\varphi, \cos\varphi)$, that is perpendicular to $\mathbf{p}$, ζ_r is a rotational friction coefficient, and $\mathbf{e}_z$ is the out of plane unit vector: $\mathbf{e}_z = \mathbf{p} \times \mathbf{t}$. The component of the Brownian force (applied on the bead) in the rod direction ($\mathbf{p}$) affects neither the rotational velocity nor the extra-stress as we will prove later. Thus, for practical applications we could simply write:

$$\mathbf{F}_{rand} = \frac{\zeta_r}{2L} \Re\left(0, \sqrt{\frac{2D_r}{\Delta t}}\right) \mathbf{t} \qquad (16)$$

Obviously, using the expression (16) for the force applied on the beads originated by the Brownian effects, and enforcing the equilibrium, we can derive the expression of the rotational velocity that involves the sum of the Jeffery term (7) plus the random contribution (14).

Now, the presence of the random forces (16) affects the virial stress expression, whose general form (when only drag and Brownian effects are considered) writes[3] [1]:

$$\boldsymbol{\tau} = 2\eta N_p \mathbf{D} : {}^4\mathbf{a} + C\left({}^2\mathbf{a} - \frac{\mathbf{I}}{d}\right) \qquad (17)$$

where η is the fluid viscosity, N_p is a coefficient depending on the fiber concentration and the fiber aspect ratio, C is a constant, $d = 2$ in 2D or $d = 3$ in 3D, $\mathbf{I}$ is the unit matrix and ${}^2\mathbf{a}$ and ${}^4\mathbf{a}$ are the second and fourth order orientation tensor:

$$\begin{cases} {}^2\mathbf{a} = \langle \mathbf{p} \otimes \mathbf{p} \rangle \\ {}^4\mathbf{a} = \langle \mathbf{p} \otimes \mathbf{p} \otimes \mathbf{p} \otimes \mathbf{p} \rangle \end{cases} \qquad (18)$$

[2] As the connector tension must equilibrate precisely the one coming from the drag, we can use in the virial stress expression directly the drag force with opposite sign.

[3] This expression will be deduced in section 3.

proving the symmetry of the extra-stress tensor.

- Taking into account external torques. When an external torque is applied, it can be represented as two forces applied on the dumbbells (having the same intensity and opposite directions). Now, the equilibrium of torques allows computing the tube rotational velocity and the bead equilibrium leads to the connector tension which appears in the stress expression. However, in this case the resulting extra-stress tensor becomes non-symmetric, inducing some interpretation difficulties that needs more in deep analyses.

3 MORE ON THE EXTRA-STRESS TENSOR

The first term of Eq. (17) can be easily obtained from Eq. (13). Thus, in what follows we focus in the second term, assuming for the sake of simplicity that the suspension involves a single tube initially aligned on the *x*-axis, i.e. $\mathbf{p}_0^T = (1,0)$, and that the solvent fluid is at rest. The averaged value of the *x*-component of the random forces acting on each bead vanishes. On the contrary, the *y*-component produces a small rotation θ of the tube. Thus, with $\mathbf{p}^T = (\cos\theta, \sin\theta)$, and focusing in the *y*-component of the random force $\mathbf{R}^T = (0, \Re)$, the extra-stress tensor writes [2]:

$$\boldsymbol{\tau} = -(\mathbf{R}\cdot\mathbf{p})\mathbf{p}\otimes\mathbf{p} + \mathbf{R}\otimes\mathbf{p} = \\ = \begin{pmatrix} -\Re\sin\theta\cos^2\theta & -\Re\sin^2\theta\cos\theta + \Re\cos\theta \\ -\Re\sin^2\theta\cos\theta & \Re\sin\theta\cos^2\theta \end{pmatrix} \quad (19)$$

from which we can conclude the traceless property of $\boldsymbol{\tau}$. When a population of tubes is considered, all of them initially oriented in the *x*-axis, the averaged expression of (19) leads to the symmetry of $\boldsymbol{\tau}$ because $\langle \Re\cos\theta \rangle = 0$. Moreover, taking into account that $\Re\sin\theta \geq 0$, the averaging of (19) writes:

$$\boldsymbol{\tau}^{\varphi=0} = \begin{pmatrix} \frac{C}{2} & 0 \\ 0 & -\frac{C}{2} \end{pmatrix} = \frac{C}{2}\hat{\mathbf{I}} \quad (20)$$

Now, for a population of tubes aligned in a generic direction φ the extra-stress tensor is obtained by rotating tensor (20):

$$\boldsymbol{\tau}^{\varphi} = \frac{C}{2}\mathbb{S}^T\hat{\mathbf{I}}\mathbb{S}; \quad \mathbb{S} = \begin{pmatrix} \cos\varphi & \sin\varphi \\ -\sin\varphi & \cos\varphi \end{pmatrix} \quad (21)$$

that after some simple manipulations and an averaging in the φ coordinate results in Eq. (17).

By prescribing the strain $\gamma(t) = \gamma_0\cos(\omega t)$ (the associated strain rate being $\dot{\gamma}(t) = -\gamma_0\omega\sin(\omega t)$) one could compute the shear stress τ_{xy} and the related rheological modulus:

$$G' = \frac{\tau_{xy}}{\gamma_0}\cos\delta; \; G'' = \frac{\tau_{xy}}{\gamma_0}\sin\delta \quad (22)$$

where δ is the phase angle between the applied strain and the stress response.

4 MORE SOPHISTICATED MODELS

Recently we have proposed some more sophisticated models. One of them lies in incorporating an electrostatic repulsive force between tubes that results in an electrostatic torque that is introduced in the procedure previous described. The other model accounts for the tube bending. This effect was modelled by assuming the tube consisting of a number of segments whose mutual rotation was restricted by incorporating a spring.

5 CONCLUSIONS

All the models until now considered exhibit elastic effects that vanish as the strain rate increases, because at high shear rates the tubes tend to rotate affinely with the flow (the other effects being negligible with respect the hydrodynamic drag). Thus a modulus G' decreasing with the frequency is found at high frequencies, in contrast with the experimental measures in which the elastic modulus increases with the strain frequency. Thus, further modelling developments must be needed.

REFERENCES

1. R.B. Bird. C.F. Curtiss, R.C. Armstrong and O. Hassager, *Dynamic of polymeric liquid, Volume 2: Kinetic Theory*. John Wiley & Sons (1987).
2. P. Grassia and J. Hinch, Computer Simulation of Polymer Chain Relaxation via Brownian motion. J. Fluid Mech., 308 (1996) 255-288.