LINEAR VISCOELASTICITY OF DISCOTIC MESOPHASES

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Introduction

Natural and synthetic mesophase pitches are discotic nematic liquid crystals and precursor material used in the manufacturing of high performance carbon fibers, by the melt spinning process [1]. Improvements in carbon fiber quality require a better understanding of the rheology and processing flows of discotic nematic liquid crystals [2]. The uniaxial discotic nematic liquid crystals are characterized by an average molecular orientation represented by the director vector **n**. In this phase the unit normals to the disk-like molecules orient close to the director **n,** see Fig. 1 [3].

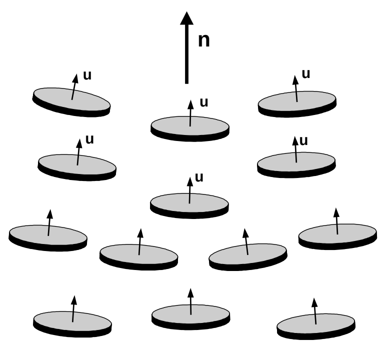

Figure 1. Discotic nematic liquid crystal showing the unit normal vector (**u**) that describes the disk-like molecules orientation and the average molecular orientation (**n**).

Small amplitude oscillatory flow is a rheological tool used to characterize linear viscoelasticity, in terms of storage G'(ω) and loss G"(ω) moduli as a function of frequency ω. Characterization through small amplitude oscillatory flows can provide useful information on steady capillary Poiseuille flow, since the terminal frequency (ω→0) response in the oscillatory flow is equivalent to the steady state behavior at infinitesimal pressure drops [4].

Discotic mesophase organization and order arises in synthetic and natural carbonaceous mesophases. Due to the practical industrial importance of this complex material some experimental results on oscillatory rheometry of mesophase pitches can be found in the literature [5]. Despite the fact that this material exhibits orientation defects (desclinations), the results show in many cases a classical Newtonian behavior for low frequencies and visco-elastic behavior for high frequencies.

Governing Equations

In this study we use the Ericksen Leslie theory [2,6,7] to investigate the small amplitude oscillatory capillary Poiseuille flow, described in Fig.2; here the Ericksen number (i.e. dimensionless pressure drop) oscillates as $E^* = E_0 \sin \tilde{\omega}\tilde{t}$, where $E_o = R^3 \left(-dp/dz\right)/K_{11}$ is the infinitesimal dimensionless amplitude and $\tilde{\omega} = \omega\left(R^2 \langle\eta\rangle\right)/K_{11}$ is the dimensionless frequency; the frequency ω is scaled with the orientation time scale $\tau_o = \left(R^2 \langle\eta\rangle\right)/K_{11}$.

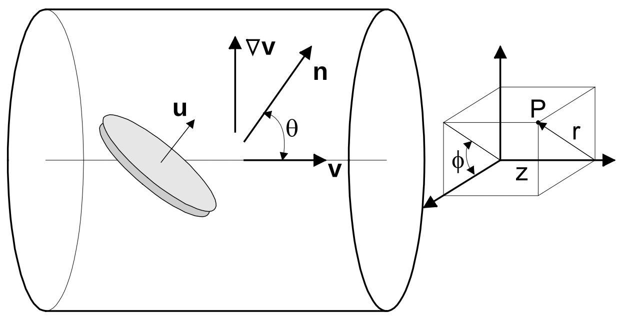

Figure 2. Cylindrical (r,ϕ,z) coordinate system used to describe a generic point P and one uniaxial disc-like molecule and the director vector (n), the velocity vector (v), the velocity gradient (∇v), and the tilt angle (θ) that gives the average molecular orientation.

Linearizing the director components of the dimensionless Ericksen-Laslie equations around the axial direction (i.e., $\sin\theta \cong \theta$, and $\cos\theta \cong 1$) the governing equations simplify to [8,9]:

$$\frac{\partial\theta}{\partial\tilde{t}} = \frac{1}{\tilde{\eta}_{splay}}\left[\frac{\partial}{\partial\tilde{r}}\left(\frac{1}{\tilde{r}}\frac{\partial}{\partial\tilde{r}}\left(\tilde{r}\theta\right)\right) + \frac{\tilde{\alpha}_3}{2\tilde{\eta}_1}E^*\tilde{r}\right] \quad (1)$$

$$\frac{\partial\tilde{v}}{\partial\tilde{r}} = -\frac{1}{2\tilde{\eta}_1}\left(E^*\,\tilde{r} \; + \; 2\tilde{\alpha}_3\frac{\partial\theta}{\partial\tilde{t}}\right) \quad (2)$$

where, $\tilde{t} = K_{11}t/\left(R^2\langle\eta\rangle\right)$ is the dimensionless time, $\tilde{v} = \langle\eta\rangle R\, v/K_{11}$ is the scaled axial velocity, $\tilde{r} = r/R$ is the dimensionless radius, $\eta_{splay} = \tilde{\gamma}_1 - \tilde{\alpha}_3{}^2/\tilde{\eta}_1$, is the re-orientation viscosity associated with the splay deformation, γ_1 is the rotational viscosity, η_1 is the Miesowicz shear viscosity, and $\tilde{\alpha}_3{}^2/\tilde{\eta}_1$ is the backflow viscosity.

The boundary conditions are as follows: $\theta(1,\tilde{t}) = 0$, $\theta(0,\tilde{t}) = 0$, $\tilde{v}(1,\tilde{t}) = 0$. Equations (1) and (2) are solved using separation of variables [9]. The simulations are performed using a set of characteristic viscoelastic material parameters listed in Table 1, which correspond to the six scaled Leslie coefficients calculated to carbonaceous mesophase [10].

Table1: Leslie viscosities coefficients for mesophase pitch [10]

Dimensionless Leslie viscosities coefficients $(\tilde{\alpha}_i = \alpha_i / \langle\eta\rangle)^*$					
$\tilde{\alpha}_1$	$\tilde{\alpha}_2$	$\tilde{\alpha}_3$	$\tilde{\alpha}_4$	$\tilde{\alpha}_5$	$\tilde{\alpha}_6$
3.6289	0.046800	0.66500	2.0270	-0.54000	0.17200

Results and Discussion

The viscoelastic material functions for the discotic mesophase are given by the complex modulus $\tilde{G}^*(\tilde{\omega}) = \tilde{G}'(\tilde{\omega}) + iG''(\tilde{\omega})$ or equivalently by the complex viscosity $\tilde{\eta}^*(\tilde{\omega}) = \tilde{\eta}'(\tilde{\omega}) - i\tilde{\eta}''(\tilde{\omega})$. To compute the dimensionless complex viscosity and complex modulus, the dimensionless flow rates $(\tilde{Q}_i, \tilde{Q}_o)$ associated with the dimensionless velocity components $(\tilde{v}_i, \tilde{v}_o)$ need to be evaluated. Thus dimensionless oscillatory flow-rates are given by

$$\tilde{Q}^*(\tilde{\omega}, \tilde{t}) = \tilde{Q}_i(\tilde{\omega}) \sin \tilde{\omega}\tilde{t} + \tilde{Q}_o(\tilde{\omega}) \cos\tilde{\omega}\tilde{t} \tag{3}$$

and

$$\tilde{\eta}' = \frac{\tilde{G}''}{\tilde{\omega}} = \frac{\pi E_0}{8} \frac{\tilde{Q}_i}{\left(\tilde{Q}_i^2 + \tilde{Q}_o^2\right)}, \qquad \tilde{\eta}'' = \frac{\tilde{G}'}{\tilde{\omega}} = \frac{\pi E_0}{8} \frac{\tilde{Q}_o}{\left(\tilde{Q}_i^2 + \tilde{Q}_o^2\right)} \tag{4}$$

Figure 3 shows the real ($\tilde{\eta}'$) and imaginary ($\tilde{\eta}''$) dimensionless viscosity components as a function of the dimensionless frequency ($\tilde{\omega}$). The real component displays three regions, with low and high frequency plateaus and a power law intermediate region. The imaginary component is non-zero at the intermediate frequency region. At low and high frequencies the response of the discotic mesophase is viscous. The discotic mesophase is viscoelastic at intermediate regions.

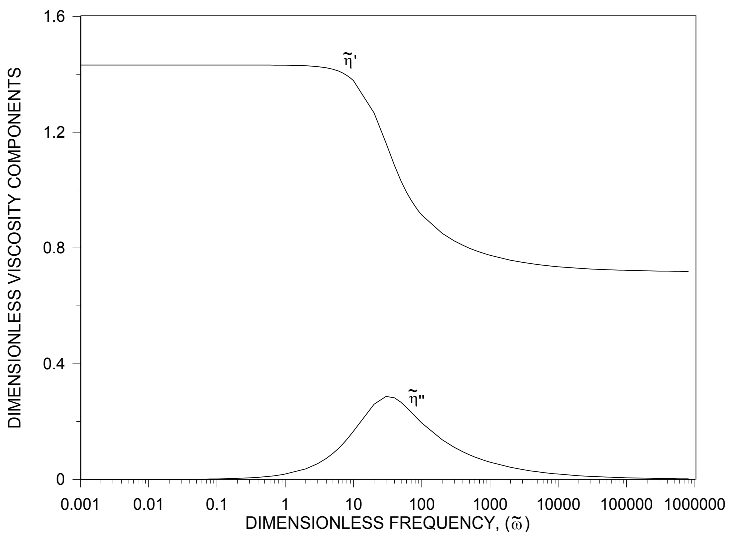

Figure 3. In-phase ($\tilde{\eta}'$) and out-phase ($\tilde{\eta}''$) dimensionless viscosity components as a function of the dimensionless frequency ($\tilde{\omega}$).

Figure 4 shows the dimensionless moduli ($\tilde{G}''$ and $\tilde{G}'$) as a function of the dimensionless frequency ($\tilde{\omega}$). The low frequency (terminal) regime is classic of a viscous fluid. The loss modulus is always greater than the storage modulus. The characteristic slopes are:

$$\text{as } \tilde{\omega} \to 0, \quad \tilde{G}' \sim \tilde{\omega}^2,\ \tilde{G}' \sim \tilde{\omega}; \text{as } \tilde{\omega} \to \infty, \quad \tilde{G}' \sim \tilde{\omega}^{1/2},\ \tilde{G}'' \sim \tilde{\omega} \qquad (5)$$

The transition region is centered around $\tilde{\omega} \approx 50$, where maximal elastic storage occurs. The figure again indicates that viscoelasticity exists when the input frequency $\tilde{\omega}$ is close to the orientation time scale τ_o.

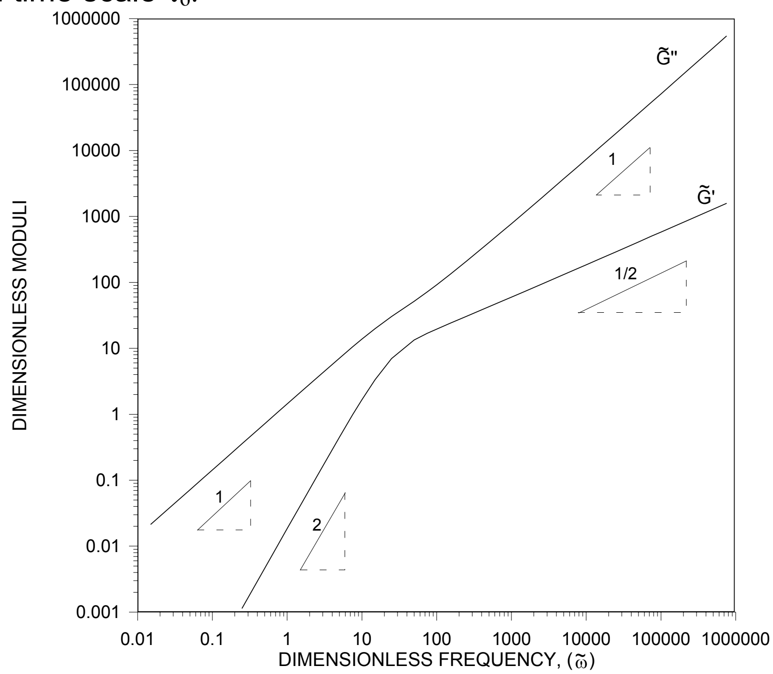

Figure 4. Dimensionless storage ($\tilde{G}'$) and loss moduli ($\tilde{G}''$) as a function of dimensionless frequency ($\tilde{\omega}$).

Figure 5 shows the phase-lag ($\delta = \tan^{-1} \tilde{G}''/\tilde{G}'$) as a function of the dimensionless frequency ($\tilde{\omega}$). The response is characteristic of a viscoelastic material with a single relaxation time. The discotic mesophase is viscoelastic ($\delta<\pi/2$) at intermediate frequencies and purely viscous ($\delta=\pi/2$) at small and large frequencies.

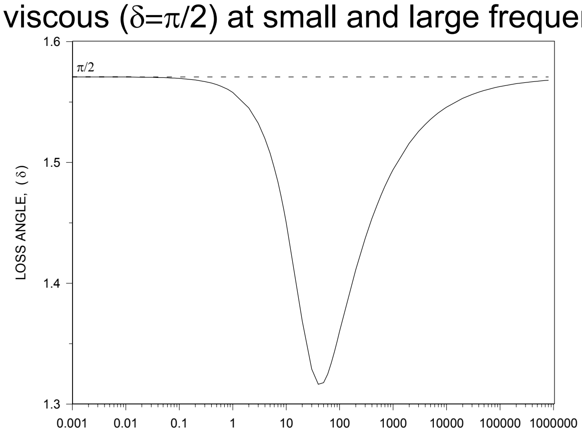

Figure 5. 'Loss angle' (δ) as a function of the dimensionless frequency ($\tilde{\omega}$)

Conclusions

Analysis and simulation of the Ericksen-Leslie equations applied to small-amplitude oscillatory capillary Poiseuille flow of defect-free discotic mesophases shows that these materials are viscoelastic only at frequencies comparable to the orientation relaxation time. At lower or higher frequencies the behavior is essentially viscous. The origin of elasticity is the orientation gradients. In the terminal low frequency region the storage modulus scales as $G' \sim \omega^2$, and the loss modulus $G'' \sim \omega$.

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