Shear Dynamics of Aqueous Suspensions of Cellulose Whiskers

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ABSTRACT: The rheology of rigid rod cellulose whisker suspensions has been investigated. The isotropic-at-rest suspension flow curves show two plateaus, one at low shear rates and another at high shear rates, that reflect the flow of isotropic (at low shear rates) or oriented (at high shear rates) suspensions. From the low shear rate viscosity plateau vs concentration, we see that the system is in the semidilute region above 0.02 wt %, in agreement with the theoretical predictions. From the same curve, we can estimate a maximum packing concentration of whiskers rods that corresponds to the experimentally measured isotropic-to-anisotropic transition. The high shear rate plateau viscosity data show that the suspension is still in the dilute state above 0.6 wt %. The critical concentration at the dilute−semidilute transition is thus strongly dependent on the state of order, which suggests that care has to be taken when measuring parameters extracted from flowing solutions or suspensions, as for example occurring with Ubbelhode viscometry. Above a certain critical concentration, the suspensions become anisotropic at rest. The viscosity vs concentration curve has a maximum that vanishes at high shear rates as for liquid crystalline polymer solutions. Rheological and rheo-optical observations show fast inception and relaxation of both the rheological functions and the texture, in complete contrast with liquid crystalline polymer solutions.

Introduction

The shear rheology of suspensions of long rigid rods has attracted attention since it is one of the simplest geometry of particle (with the sphere). The main difference with the sphere is that the description of the flow of long rods must include an orientation function that both depends on the flow and influences the flow. To that respect, the flow of spheres is much simpler. Several different concentration regions can be found for a suspension of rods at rest.[1] The dilute case, defined for *volume fraction* $< d^2/L^2$, is the simplest. In this regime, the rods are not interacting, and most functions scale with the concentration. The semidilute and concentrated regions are more difficult to describe since rods are interacting, leading to synergetic effects. For example, the rotational relaxation time scales with the square of the concentration in the semidilute regime.

The rheology of rod suspensions has been mainly described in molecular terms to calculate the intrinsic viscosity in the case of randomly oriented rods, and the stress in simple flows (shear and elongation). The flow at high flow shear rates is complicated since it must take into account hydrodynamic and anisotropic hindrance interactions.[1−4] Comparison between experiments and theory with rigid rods are rather scarce and are mainly restricted to measurements in slow flows. Several papers are studying the shear viscosity of cellulose or chitin crystallites.[5−7] The first papers[5,6] studied the hydrodynamic properties comparing intrinsic viscosity, flow birefringence, and light scattering, stressing the influence of ultrasonic treatments on the change of crystallite length. The last paper on chitin crystallite[7] suspensions describes the viscosity curves in the isotropic and anisotropic regimes. The isotropic suspensions have a shear thinning region, without any detectable Newtonian regime.

The anisotropic suspensions have a three-zone shape similar to nematic polymer liquid crystals. No indication is given if this is due to a tumbling type of flow. The rheology in the nematic region of rigid rod suspensions has not been often described, despite the fact that the rheology of nematic polymer solution is well documented, both in terms of experiments and theories.[8] These polymer solutions are composed of rigid or semirigid Brownian molecules that are organising themselves above a certain concentration to form a nematic phase. Two types of behavior can appear in shear depending on the ratio of two Leslie viscosities, either flow-aligning, where the director adopts a stable position during flow, or tumbling, where the director has no stable position. This last effect is supposed to be linked to the occurrence of a negative first normal difference.[9] The strong influence of the texture (i.e., how the director is arranged in space) on the flow leads to extremely long transients (several hundred shear units are common) and a scaling of most transient functions with the amount of strain.[10]

The purpose of this article is to investigate the shear rheology of cellulose whiskers (which are a good example of long rigid rods) in aqueous suspension, taking into account the effect of orientation. The goal is to see whether the effects of the shear-induced orientation that should occur in the dilute and semidilute regime can be measured and described. For the most concentrated suspensions that are in a liquid crystalline state, the rheological behavior will be compared with the case of nematic polymer solutions.

Cellulose whiskers can be prepared easily from several natural sources in the form of micronlike rods with a length over diameter (L/d) ratio in excess of 100. Potential applications for composite reinforcement[11,12]

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promoted interest in the study of such suspensions. Revol et al.[13,14] studied the phase separation and the magnetic field orientation of such whiskers suspended in water. The suspensions are cholesteric above a certain critical concentration of whiskers, probably due to a twisting of the whiskers.[15] Below this critical concentration, the suspensions are isotropic at rest. In a magnetic field, the ordered phase becomes oriented with its cholesteric axis parallel to the applied field. Upon shearing, the suspensions go from cholesteric to nematic.[15] Recently, the shape and lateral dimensions of the cellulose monocrystals were measured.[16]

The manuscript will first examine the shear rheology of suspensions that are isotropic at rest, considering the measurement of intrinsic viscosity, the influence of the shear rate on the viscosity and the dependence of viscosity on concentration when the rods are randomly or well oriented by the flow. In the second part, the rheology of the anisotropic-at-rest suspensions will be studied.

Experimental Section

Preparation of the Cellulose Whiskers Samples. The whiskers were prepared by sulfuric acid hydrolysis of cellulose fibers coming from the cellulose tunic of sea animals (*Microcosmos fulcatus*).

The proteins were extracted by three successive bleaching treatments. The tunicin were then disintegrated in water with a Waring Blendor at a concentration of 5 wt % (3−4 runs of 10 min). The resulting aqueous tunicin suspension was homogeneous and was submitted to a hydrolysis with H_2SO_4 65 wt % at 80 °C for 25 min, under strong stirring. After this was washed many times with water and centrifuged (30 min at 14 000 rpm), the final pH was $\approx$ 5. The suspension was dispersed by sonication and then neutralized and washed by dialysis until the water outside the dialysis membrane was neutral. The resulting suspension was treated with a mixed-bed ion-exchange resin (this mixture was kept at room temperature for 3 days) and dispersed by an ultrasonic treatment. Then, the suspension was concentrated by dialysis using a high molecular weight poly(ethylene glycol) (M_w = 35 000) concentrated solution and dispersed again by an ultrasonic treatment. Finally, a stock suspension with 3.5 wt % cellulose concentration was prepared.

Samples with different concentrations were carefully prepared by diluting the stock suspension with highly purified water and the resulting suspensions were dispersed by sonication. The concentration (c, wt %) of the prepared samples for the rheological investigations varies from 0 to 3.5 wt %. Volume fractions (ϕ) were calculated as a function of the weight fractions (ϕ_w)

$$\varphi = \frac{\rho_1 \phi_w}{\phi_w(\rho_1 - \rho_2) + \rho_2} \tag{1}$$

where $\rho_1 = 1$ g/cm^3 and $\rho_2 = 1.52$ g/cm^3 are the densities of the continuous phase (water) and dispersed phase (cellulose), respectively.

The dimensions of the prepared whiskers were measured by transmission electron microscopy (Philips EM400T). A dilute whiskers suspension was deposited on a carbon-coated grid and observed by TEM. The individual rod lengths were in the range of 0.2 to several micrometers with a mean length $L = 2.1$ μm (Figure 1). The average diameter d was found to be 15 nm. This gives a mean L/d ratio of 140, with a rather large dispersity. An elemental analysis gave a content of one sulfate group per nine structural units,[17] i.e., about 760 sulfate groups per rod.

Rheology and Rheo-optics. The intrinsic viscosity measurements were carried out in water at 25 °C (±0.01 °C) by use of an Ubbelohde level viscometer. The flow volume of the viscometer was ~10 mL, making drainage errors unimportant. Flow times were obtained with an accuracy of ±0.01 s. The flow time for water was 98.82 s. For concentrations lower than 2.5 wt %, the viscosity measurements were carried out with a Contraves Low Shear 30, in the $10^{-2} < \dot{\gamma} < 10^2$ shear rate range. For higher concentrated suspensions, the viscosity was measured with a RMS 800 Rheometrics rheometer (40 mm cone and plate, cone angle of 2°). The investigated shear rate range was $10^{-3} < \dot{\gamma} < 10^{-2}$ s^{-1}. The system was equipped with a special installation to saturate the atmosphere with water.

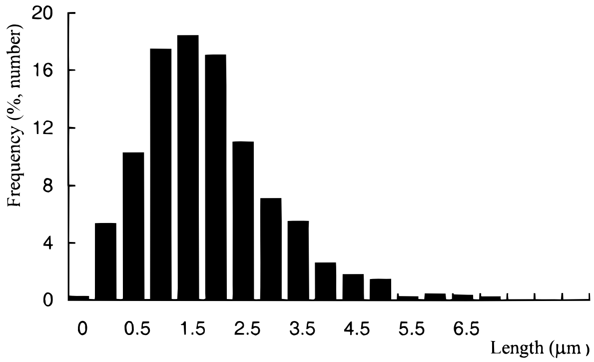

Figure 1. Length distribution of the cellulose whiskers.

Rheo-optical experiments (optical microscopy and light scattering) were performed with a cone and plate transparent rheometer previously described.[18]

All viscosity and rheo-optical experiments were performed at 25 °C.

Results and Discussion

Solution Characterization. The critical concentrations of the dilute−semidilute and semidilute−concentrated transitions of the cellulose whiskers suspended in water can be calculated using the rigid rod approximation and the mean values of length and diameter:

$$\varphi^* = d^2L/L^{-3} \tag{2}$$

$$\varphi^{**} = d^2L/L^2d \tag{3}$$

For an axial ratio of 140, as investigated in this work, the boundary between the dilute and semidilute regimes is $c = 0.0076$ wt % (or 0.005 vol %), and the boundary between the semidilute and the concentrated is $c = 1.08$ wt % (or 0.71 vol %). When rods are long enough, they macroscopically orient in a nematic phase above a certain concentration, c = 3.6 wt % or 2.4 vol % according to the Onsager theory[2] and c = 8.3 wt % or 5.6 vol % according to the Flory theory.[3] By optical microscopy in crossed polarization geometry, the first birefringent domains appear around $c = 0.8$ wt %. More diluted suspensions are completely isotropic at rest. Above this limit, there is a biphasic suspension up to about 2.5 wt % where the suspension seems fully anisotropic.

The intrinsic viscosity was measured from the relative viscosity obtained with the Ubbelohde viscometer. The suspension viscosity vs concentration is plotted in Figure 2 with the fit proposed by Fedors[19]

$$\frac{1}{2(\eta_{\rm rel}^{1/2} - 1)} = -\frac{1}{[\eta]c_{\rm m}} + \frac{1}{[\eta]c} \tag{4}$$

where $\eta_{\rm rel}$ is the relative viscosity ($\eta_{\rm rel} = \eta/\eta_0$, η_0 being the viscosity of the water) and $c_{\rm m}$ is the maximum packing density of the rods. The fit of the experimental

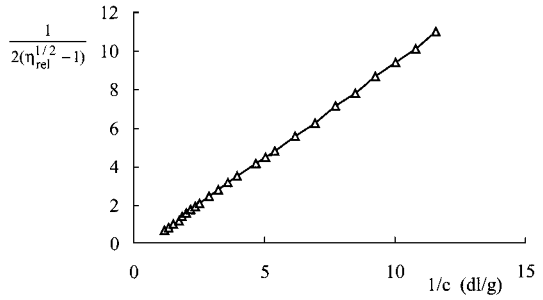

Figure 2. Fedors plot (eq 4) for cellulose whiskers suspensions in water at 25 °C.

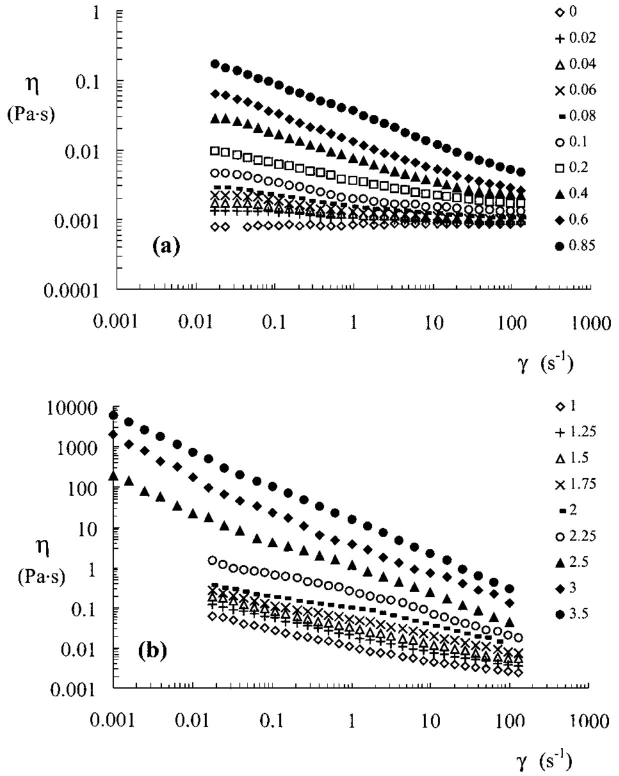

Figure 3. Viscosity vs shear rate for the suspensions of whiskers at different concentrations of cellulose (wt %).

data with eq 4 gives an intrinsic viscosity $[\eta]$ of 1.03 dL/g, that can be compared to $[\bar{\eta}] = 1.09$ dL/g if one would have used the Huggins[20] or the Schulz–Blaschke[21] equations.

The packing parameter c_m, calculated from eq 4, is proportional to the maximum volume fraction to which rigid particles can pack, ϕ_m. The value of ϕ_m can be calculated from $\phi_m = kc_m$ and $2.5k = [\eta]$. In our case the c_m value is 2.463 g/dL and ϕ_m is found to be around 1, which seems too high. Keeping in mind that viscosity data measured with the Ubbelohde technique are performed at high shear rates, these data will be discussed in the next section.

Rheology in the Isotropic-at-Rest Regime (c < 0.8 wt %). This regime goes from 0 to 0.8 wt % and comprises the dilute and semidilute regimes. Figure 3 shows the viscosity vs shear rate curves for the whole range of accessible concentration, 0–3.5 wt %. We are here interested in the concentrations below 0.8 wt %. Two different regimes can be seen.

The first regime spans from 0 to 0.4%. Its main characteristic is that the curves have two plateaus, one at low shear rate, and another one at high shear rates. The 0.4 wt % limit must not be considered here as a real physical boundary, but is only due to the difficulty of conducting experiments at high shear rates for the most concentrated suspensions. The plateau at low shear rate where the viscosity does not depend on the shear rate is the true Newtonian viscosity. In this region of low shear rates, the rods keep a random orientation. The plateau at high shear rates reflects the other extreme case, where the rods are oriented in a steady-state manner. According to Doi and Edwards,[1] dilute solutions of rods reach an asymptotic limit of an order parameter of $^2/_3$. Neutron scattering measurements of the order parameter during flow gives a limiting order parameter of about 0.8 for more concentrated suspensions of much smaller cellulose whiskers rods, with a rod orientation in the direction of the flow.[15] The rods are well oriented in this region and an increase of shear rate in the region does not change the mean rod orientation and thus does not change the viscosity.

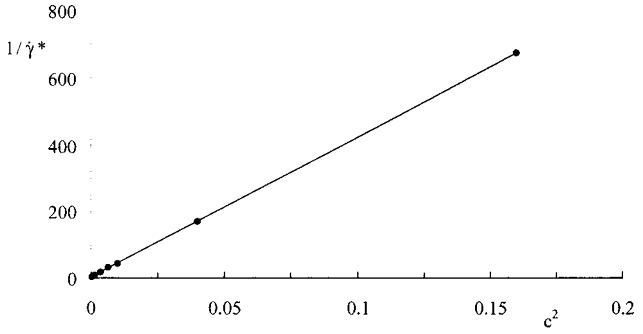

Figure 4. Plot of $1/\dot{\gamma}^*$ vs c^2.

From Figure 3, it can be seen that there is a clear transition at the end of the Newtonian plateau. This is true at least for the concentrations up to 0.1 wt %. This critical shear rate $\dot{\gamma}$ correspond to the inverse of the rotational diffusion time τ_{rot}. According to Doi and Edwards,[1] τ_{rot} can be expressed in the semidilute regime as

$$\tau_{rot} = \frac{\tau_{rot,0}(\nu L^3)^2}{\beta} \tag{5}$$

where ν is the number of rods per volume $\nu = (\vartheta/M)N_A$ (considering ϑ the weight of polymers in unit volume of the solution) and $\tau_{rot,0}$ is the rotation diffusion time in the dilute regime:

$$\tau_{rot,0} = \frac{\pi\eta_s L^3}{3(\ln(L/d) - 0.8)} \tag{6}$$

A plot of the inverse of the critical shear rate $\dot{\gamma}^*$ vs the square of the concentration is shown in Figure 4. It shows that eq 5 is obeyed. Using eqs 5 and 6, it is possible to estimate the coefficient β to be 3.2×10^3, in good agreement with other experimental data.[1]

We extrapolated the straight line of Figure 4 to calculate the critical shear rates of two other concentrations, 0.2 and 0.4 wt %, where the transition was just out of the experimental range of shear rates. From Figure 3, the Newtonian viscosities of the 0.2 and 0.4 wt % suspensions were estimated to be 0.0105 and 0.0312 Pa·s, respectively.

The concentrations up to 0.4 wt % show two plateaus, at low and high shear rates. Figure 5 shows how these viscosities are a function of rod concentration. For the

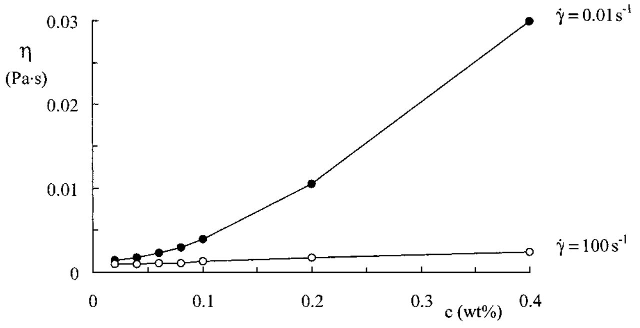

Figure 5. Viscosity as a function of rod concentration for $\dot{\gamma} =$ 0.01 and 100 s^{-1}.

Newtonian plateau, the two highest points are coming from the extrapolation described above. The viscosity at the Newtonian plateau increases strongly with concentration. The viscosity at the high shear rate plateau (in fact taken at $\dot{\gamma} = 100$ s^{-1}), is linear with concentration. Extrapolation to zero concentration allows a calculation of the intrinsic viscosity. Both plateau gives similar results, $[\eta]_{\mathrm{Newtonian}} = 1.13$ dL/g and $[\eta]_{100\mathrm{s}} = 0.98$ dL/g. These values are very close to the one deduced from Ubbelohde viscometry (1.03 dL/g), showing the consistency of these approaches.

The Newtonian viscosity vs concentration curve was fitted with a classical, empirical suspension theory expression:

$$\eta_{\mathrm{rel}} = \left(\frac{1 - c}{c_{\max}}\right)^{-2} \tag{7}$$

The $c_{\max}$ parameter, which is the maximum packing density, was found to be 1.07 wt %. $c_{\max}$, extracted from the Newtonian viscosity, should represent the maximum packing of randomly oriented rods. This should correspond to the transition between the isotropic to the nematic suspensions. This is indeed what is found, the isotropic–nematic transition being observed experimentally around $c = 0.85$ wt % ($\varphi = 0.0056$).

All these data and calculations are self-consistently showing that the suspensions are in the semidilute regime for all studied concentrations. This is fully in agreement with the theoretical predictions of a dilute–semidilute transition concentration of 0.0076 wt %.

The situation is very different for the high shear rate plateau. The viscosity is linearly proportional to concentration and is much lower than the one of the Newtonian plateau (Figure 5). The lowest viscosity is clear to understand. The rods are orienting during the flow in the flow direction, as shown by neutron scattering.[15] This decreases the drag force and reduce the viscosity.

More interesting is the fact that up to 0.4 wt %, the viscosity shows a behavior typical of a dilute regime. This is due to the fact that interactions between oriented rods occur at a much higher concentration than when they are randomly oriented. The suspensions between 0.02 and 0.4 wt % are thus in the semidilute regime when studied at rest or below a shear rate lower than the inverse of the rotational relaxation time, and in the dilute regime above a second critical shear rate $\dot{\gamma}^{**}$ which marks the beginning of the high shear rate plateau. Care has to be taken when measuring intrinsic physical parameters with methods that needs a flow. This is the case of Ubbelohde viscometry, and this explains why the maximum packing concentrations calculated from these data are higher.

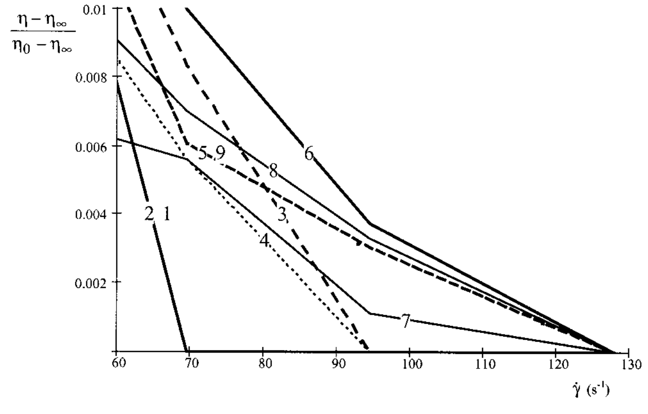

Figure 6. $(\eta - \eta_\infty)/(\eta_0 - \eta_\infty)$ as a function of $\dot{\gamma}$ for the following samples: (1) 0.02 wt %; (2) 0.04 wt %; (3) 0.06 wt %; (4) 0.08 wt %; (5) 0.10 wt %; (6) 0.20 wt %; (7) 0.40 wt %; (8) 0.60 wt %; (9) 0.85 wt %.

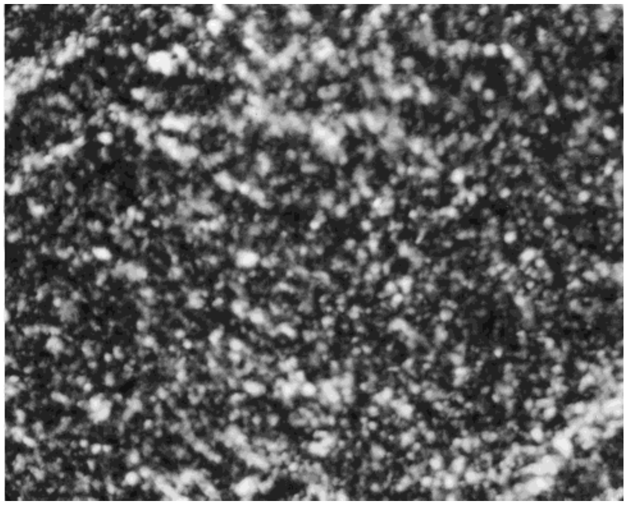

Figure 7. Optical micrograph between crossed polarizers of a 3 wt % cellulose whisker suspension.

The last data that can be obtained from Figure 3 for concentrations below 0.4 wt % are the shear rate $\dot{\gamma}^{**}$ at which the high shear rate plateau starts. An enlargement of this region shows that this plateau is not exactly reached at the maximum shear rate we used (Figure 6). It is nevertheless clear that $\dot{\gamma}^{**}$ depends on concentration, increasing slightly with concentration. We do not know how to interpret this.

Rheology in the Anisotropic-at-Rest Regime. As said before, the suspensions becomes anisotropic above $c = 0.85$ wt % ($\varphi = 0.0056$). Figure 7 shows an optical micrograph taken between crossed polarizers of a 3 wt % suspension. The suspension is anisotropic, with a domainlike aspect. The cholesteric character cannot be seen (no typical equidistant striations), probably due to the small size of the domains or of the cholesteric pitch. The $c = 0.85$ wt % concentration is far below what is predicted by the Onsager theory for the isotropic-anisotropic transition concentration for rods of $L = 2.1$ μm and $d = 15$ nm, i.e., a concentration of 3.6 wt %. A lower concentration means having a much higher axial ratio. This is difficult to understand since what has been ignored in the present calculation is the size of the ionic layer that is decreasing the axial ratio, and thus going in the opposite direction. We have no clear idea about the origin of this discrepancy, except that there might

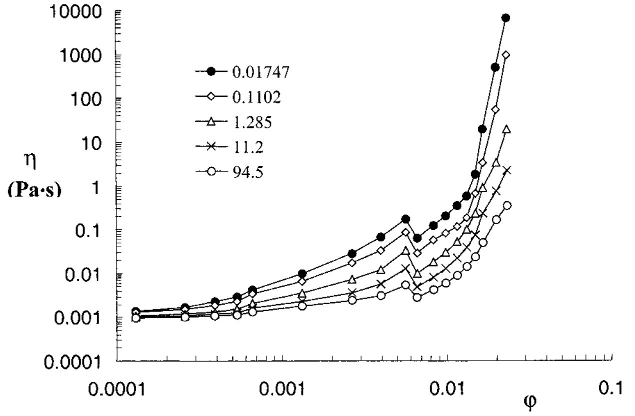

Figure 8. Viscosity, η, vs v/v fraction, φ, at the indicated shear rates (s^{-1}).

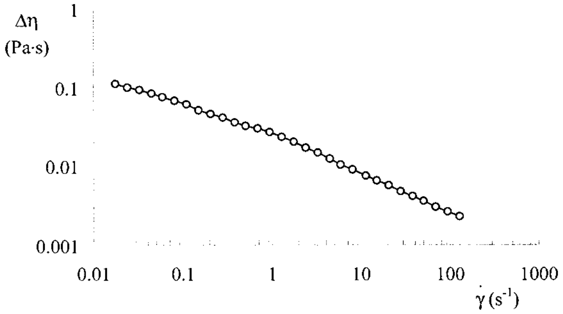

Figure 9. Difference $\Delta\eta = \eta_{0.85} - \eta_{1.00}$ vs shear rate for the suspensions of cellulose whiskers.

be a fractionation, the larger rods forming the anisotropic phase.

Part b of Figure 3 deals with anisotropic-at-rest suspensions. Contrary to the isotropic suspensions where a shear thinning region is surrounded by two plateaus, the anisotropic suspensions have plateau (more precisely a weak shear thinning zone) surrounded by two shear thinning regions, in the typical style of liquid polymer solutions.[22] LC suspensions and LC polymer solutions can be easily compared, the same main effects in terms of texture being expected.

As for solutions, there is a sudden decrease of viscosity at the transition as shown in Figure 8.

At low shear rates, the defect texture is playing a dominant role[23] and this creates the shear thinning behavior. At high shear rates, the suspension is flow aligned, and this gives a low viscosity state. This is illustrated in Figure 9 where the viscosity difference between the suspensions concentrated at 0.85% and at 1% is plotted vs shear rates. This classical result for LC polymer solutions is found here for LC whiskers suspensions. At low shear rates, the viscosity difference is large because the isotropic-at-rest suspension is disordered. At high shear rates, the viscosity difference is very small because both suspensions are ordered, the low concentrated one by the shear, the high concentrated one by the LC character and the shear. If both were fully oriented, the 1 wt % suspension should be more viscous than the 0.85% one, which is not the case here. The suspensions are not fully oriented at the highest shear rates used here, as predicted by the theory[1] and measured experimentally.[15]

The transients are very short, contrary to the classical behavior of LC solutions where hundreds of strain units are necessary to drive the fluid in a steady state, and where long times (or time multiplied by the applied shear rate) are needed to relax to a rest state. Figure 10 shows the start-up viscosity increase as a function of time for two suspensions. A few seconds are needed to establish a steady-state viscosity, i.e., less than one shear unit. This has to be compared with several tens, or hundreds of shear units necessary for LC polymer solutions.

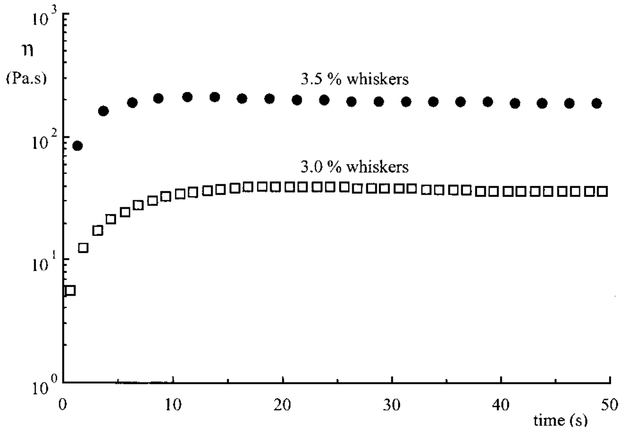

Figure 10. Evolution of the viscosity as a function of the time for a start up experiment from 0 to 0.1 s^{-1} for two cellulose whiskers suspensions.

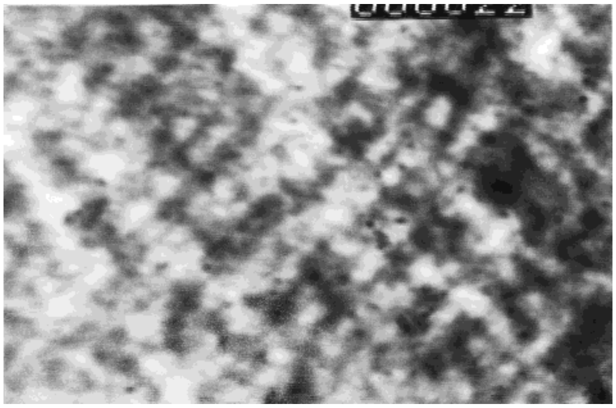

Figure 11. Optical micrograph between crossed polarizers of a suspension of a 2.5 wt % at $\dot{\gamma} = 27.7\ s^{-1}$.

Observations by optical microscopy during flow show that the concentrated suspensions (c larger than 2 wt %) goes from the at rest polydomain morphology to a morphology with sorts of bands, or periodic structure, oriented at 45° of the shear direction (Figure 11).

This band morphology occurs above a certain shear rate ($\dot{\gamma} > 1\ s^{-1}$). This behavior can be clearly seen by light scattering between crossed polarizers. In that case the scattering pattern evolves from ellipsoidal to four lobes. This is very reminiscent of the flow of LC polymer solutions.[21] In this latter case, the origin of this change is thought to be the creation and organization of defects. The relaxation from the four lobe pattern to the at rest circular pattern is very quick, in less than one second. This is in complete contrast with LC solutions, but in agreement with the quick transients seen in rheology. It is also in contrast with the recent measurements of the relaxation of the order parameter by neutron scattering.[15] This may mean that the scattering patterns are due to a relatively small number of scattering objects that have a limited spatial extension and may not contribute to the overall order parameter.

The main difficulty in these suspensions is the very quick transients that are making difficult any freezing of the flowing structure for subsequent microscopic observations, contrary to thermotropic polymers, for example.[25]

Conclusions

Suspensions of cellulose whiskers are interesting models for studying the rheology of rigid rods. They can be easily oriented and the flow properties in the disordered or ordered states can be compared. Above a certain concentration, they become liquid crystalline, with an overall texture development that is similar to LC polymer solutions.

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