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Shear Velocity Profiles in (Hydroxypropyl)cellulose Solutions

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Introduction

(Hydroxypropyl)cellulose (HPC) can form anisotropic solutions when dissolved in suitable solvents. All of them are cholesteric at rest and undergo a cholesteric to nematic transition upon shearing. These solutions have been extensively studied and their rheology is fairly well-known[1-6] although there is no established theory able to describe it. All the measurements reported so far have been classically performed with cone-and-plate, plate–plate, eccentric disk, concentric cylinder, or capillary rheometers. In the cone-and-plate geometry, for small enough gaps, the relations between force or torque and velocity to shear stress and shear rate are based on several assumptions, these being that a simple shear experiment will give a linear velocity profile and that the flow is laminar.[7]

Rheooptical experiments[8] suggest that at low shear rates, the flow of anisotropic HPC solutions is laminar, but with no indication about the velocity profile. On the contrary, recent theoretical calculations[9] predict that under the conditions where a band texture is present after cessation of shear, the flow should not be laminar but must have a complex three-dimensional velocity profile. The purpose of this work is to report measurements of the velocity profiles of isotropic and anisotropic HPC–water solutions in simple shear at various shear rates. This is necessary for measuring a meaningful viscosity. In addition, it will be possible to compare the velocity profiles for anisotropic solutions to theoretical predictions when available.

Experiments

The rheological data (viscosity and first normal stress difference) were obtained with an Instron 3250 cone-and-plate rheometer. Velocity profiles were determined with custom-made optical equipment adapted to the Instron 3250, which is described elsewhere.[8] Two HPC (Hercules)–water solutions (M_w = 100 000, 30% by weight, isotropic; 55% by weight, anisotropic) were prepared with the usual procedure,[8] except that a few percent by volume was filled with well-calibrated polystyrene spheres (diameter 9.89 μm, National Bureau of Standard Reference Material 1960). The spheres were used as velocity tracers. We checked that the moving spheres did not perturb the flow by looking carefully at the birefringence around the tracer sphere in the anisotropic solution with crossed polarizers. Any perturbation such as a flow around the sphere, meaning that the sphere moved slower than the surrounding fluid or rotated, would have been immediately detected.[10] The spheres could then be considered as moving at the same speed as the surrounding fluid. The vertical position of a tracer between the cone and the plate was determined by focusing the microscope. The distance between the cone and the plate was 350 μm at the point where the measurements were performed.

The velocity was measured manually with a chronometer, and this limited the available shear rates to a maximum of 4 s^{-1}. The dispersity of the measurements was ca. 15%. The velocity measurements were conducted without polarizers to allow a good focus on the individual tracer spheres. Velocity measurements were done at several shear rates. In particular with the anisotropic solution, we tried to investigate low shear rates where the HPC solution does not lose its texture either in shear or when the shear is stopped or at higher shear rates ($\dot{\gamma} \geq 1.1$ s^{-1}) where the texture is strongly modified by the flow and where band textures appear after cessation of shear.[5,8] The values of the shear rates reported herein are calculated assuming a linear velocity profile in the usual way and are thus termed apparent. The shear deformation imposed on the sample was always larger than 100 shear units when the measurements were performed.

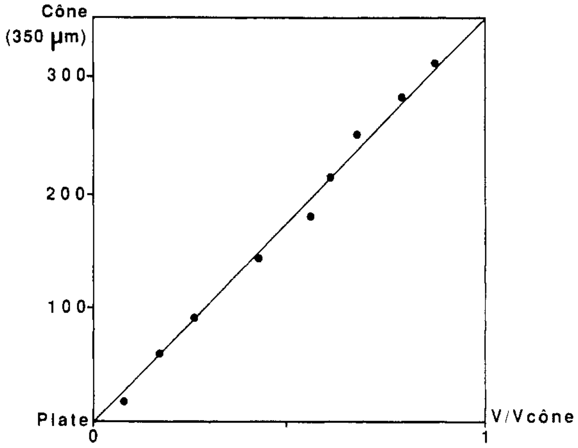

Figure 1. Reduced velocity V/V_{cone} profile for the HPC isotropic solution. The shear rate γ is 0.75 s^{-1}. The cone velocity V_{cone} is 0.26 mm/s.

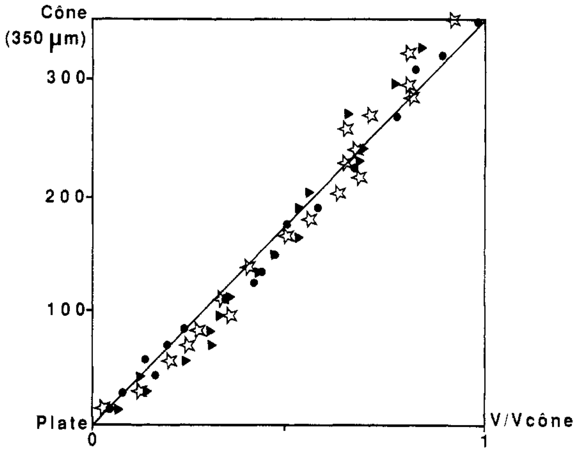

Figure 2. Reduced velocity V/V_{cone} profiles for the HPC anisotropic solution: (☆) V_{cone} = 0.10 mm/s, $\dot{\gamma}$ = 0.30 s^{-1}; (●) V_{cone} = 0.26 mm/s, $\dot{\gamma}$ = 0.75 s^{-1}; (▲) V_{cone} = 0.42 mm/s, $\dot{\gamma}$ = 1.20 s^{-1}.

Results and Discussion

When the HPC solution is isotropic, it behaves as a normal viscoelastic fluid.[4] As expected, the isotropic HPC solution gave a linear velocity profile (Figure 1). Neither slip nor a stagnant layer was detected at the cone or plate. All the observed spheres moved at a constant speed, whatever their vertical position was, and there was no detectable velocity out of the plane of shear (if such a velocity existed, its value was less than 2% of the velocity of the cone). This means that the flow was laminar. This shows that this method is reliable and quantitatively correct.

The anisotropic solutions gave a different result. As for the isotropic solution, the flow was found to be laminar. All the spheres moved at a constant speed, with no acceleration or deceleration. This seems to be in contradiction with the results of ref 9, which predict a complex flow behavior. This is also an important feature that will strongly simplify numerical simulation since there seems to be no influence of the complex defect texture on the streamlines. Velocity profiles for the anisotropic solution are given in Figure 2. The profile is not linear but shows

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a small distortion near the walls. This distortion is small, but reproducible. A recent investigation[11] gave a similar result, and this velocity profile distortion could be characteristic of this class of material. Such a velocity profile does not allow, in principle, a proper determination of a viscosity. Nevertheless, the small distortion of the profile has only a small influence on the calculation of the viscosity, and this explains why viscosity measurements performed in different flow geometries (capillary and cone-and-plate) give comparable results for these anisotropic polymer solutions.[4]

The following conclusions for the anisotropic solution can be drawn from this basic experiment:

(1) The velocity profile is very similar in shape at very low cone velocity and in a range where a band texture appears after stopping shear. This suggests that the average flow mechanisms in these two regions are not basically different, despite the fact that the textures in shear and during relaxation are different.

(2) A small distortion of the velocity profile occurs. It seems to have a negligible influence on viscosity measurements. This distortion can be due to a change of the macroscopic texture or a variation of the director in the gap.

(3) The flow is laminar. This is important, especially in the low shear rate region, where the defect texture is similar to the one at rest.[12]

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