CELLULOSE CHEMISTRY AND TECHNOLOGY

COMPARISON OF ELASTICITY CONTRIBUTIONS DURING THE FLOW OF A CELLULOSE DERIVATIVE SOLUTION

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Three contributions to elasticity (chain entropic contribution, orientational distortion of the director of a nematic phase, interfacial tension) in viscoelastic fluids are compared experimentally using hydroxypropylcellulose (HPC) solutions in water. Elasticity is assessed by measuring the elastic recovery after a simple shear. The entropic contribution to elasticity is measured after shearing an isotropic concentrated solution. The contribution of orientational distortions of the director of a nematic phase to elasticity is measured on HPC-water solutions with HPC concentrations above the isotropic-nematic (or twisted nematic) concentration. Finally, an incompatible blend of HPC-water and polydimethylsiloxane is used to measure the elastic contribution due to an increase of interfacial area. Results show that by far, the elastic recovery of the distortion of a nematic director is much higher than the contribution of the entropic elasticity.

Keywords: rheology, elasticity, entropy, liquid crystal, blend, hydroxypropylcellulose

INTRODUCTION

For the large majority of materials having an elastic behaviour, elasticity is confined to a very small deformation range since elasticity is mainly due to bond deformation. However, it is well known that a class of materials, i.e. polymers, present highly elastic behaviour above their glass transition. This peculiar feature is not due to bond deformation, but to the fact that chains can change their conformation, thus modifying their entropic contribution of the free energy, which generates large elastic stresses when chains are deformed. This phenomenon is exacerbated when all chains are connected, as in rubbers. However, there are other morphological arrangements besides a polymer melt or a polymer solution, which also generate elasticity. One of them is the deformation of a liquid crystalline phase. Here, elasticity is due to the fact that the arrangement of the rather rigid, elongated molecules, which are in such liquid crystalline phases, can easily move out of the lowest state of energy in a flow. Upon cessation of the flow, there will be an elastic return to the lowest free energy state. Another situation is when there is an interface between two fluids and the flow increases the interfacial area. Again, when stopping the flow, the system will tend to minimize its interfacial area, generating an elastic response. These three contributions, (i) entropic elasticity in connected polymer chains, (ii) distortion of orientation in liquid crystalline phases and (iii) minimizing interfacial areas strongly depend on many factors, such as the type of polymer (flexibility, molar mass, for example), type of liquid crystalline phase (nematic, twisted nematic or smectic phases, for example) and interfacial tension. However, it is interesting to find orders of magnitude for these three contributions to elasticity. This is the purpose of this paper. Elasticity will be simply assessed by measuring the elastic recovery after stopping a simple shear.

The elastic recovery is the measure of the amount of deformation γ_r recovered after stopping a shear. It depends on the shear rate and on the amount of deformation imposed during shear. In this work, we will ensure that the amount of imposed deformation is large enough to lead to a stable steady state. Only the shear rate may vary the elastic recovery. The larger is the elastic energy stored, the larger will γ_r be.

A single polymer, hydroxypropylcellulose (HPC), will be placed into these three situations, first as a concentrated isotropic polymer solution to measure the contribution of entropic elasticity. The contribution of the orientational distortion of the director of nematic phases to elasticity will be measured using HPC-water solutions with HPC concentrations above the isotropic-nematic (or twisted nematic) concentration. Finally, an incompatible blend of HPC-water and poly(dimethylsiloxane) will be used to measure the elastic contribution due to an increase of interfacial area. The rheology and transport properties of hydroxypropylcellulose solutions in water have been widely studied from dilute to concentrated isotropic and liquid crystalline solutions, owing to their ease of preparation and importance in the pharmaceutical field.[1-10]

Brief description of the three elasticity mechanisms

Most single long polymer chains have a high elasticity and are very extendable under stress. The easiest way to mathematically handle large-scale deformations of a polymer chain is to consider it as a Gaussian chain, which can be seen as beads connected by a spring. Such a model allows describing the mean deformation of the chain conformations when placed in a suspending fluid. Two models have been widely used, the Rouse model where excluded volume and hydrodynamic interactions are neglected or the Zimm model where hydrodynamic interactions are taken into account. Many books provide a good description of these phenomena.[11,12] When the stress imposed to such a chain, leading to an increase of the mean end-to-end distance of the chain, is released, the chain fully recovers from the imposed deformation. Such phenomena have been directly visualized using long DNA molecules.[13,14] During the shear flow of a dilute polymer solution, all polymer chains will suffer alternative stretching and contraction. When stopping flow, all chains will return to their equilibrium end-to-end distance driven by an elastic force due to entropy. However, a dilute flexible or semi-flexible chain solution will not show any elastic recovery due to a lack of connectivity between chains, despite the fact that chains will recoil after stopping the stress having extended them. It means that elastic recovery will be only seen in the concentrated regime where temporary junctions are present, connecting all chains to the boundaries of the sample. The elastic recovery depends on many parameters intrinsic to the chain and on the type of junctions linking chains. A good discussion of the ability of models to predict the elastic recovery of polymer solutions and melts is found in the paper of Lodge.[15] The elastic recovery is a function of the applied stress and of the details of the polymer structure.

The physical situation is very different for nematic liquid crystals. Here, there is no need to have flexible polymer chains since even if the molecules are fully rigid, these phases will show elasticity and thus an elastic recovery after stopping a shear. The nematic state is an intermediate thermodynamically stable state between liquid and crystal. It has a uniaxially oriented structuration along a direction called director. If the molecules are chiral, there is a helical twist of the nematic along an axis perpendicular to the director. This phase is called twisted nematic or more commonly cholesteric. Cholesterics and nematics are the same thermodynamic state. This is the case of the HPC-water solutions studied in this work. This cholesteric order is present at rest, and is transformed into a nematic state under flow. The director, representing the mean direction of the nematic in a certain volume of the material, may not be the same in all samples. This is in fact the most probable situation and a supramolecular organization of the director is present: a polydomain structure will develop. Energetically speaking, the locations where directors with different directions meet have a prohibitive free energy cost. The molecules thus rearrange themselves to reduce this free energy and this creates positional defects or disclinations, which have well-defined topological organisations. These organisations will influence the rheological behaviour of the nematic fluid.[16] The rheology of the liquid crystals composed of small rod-like molecules was fully described by Ericksen and Leslie,[17-19] with six viscosity coefficients (a Newtonian fluid only has one). In addition, this theory takes into account the elasticity due to the distortion of the director. This elasticity is called

Frank elasticity and is associated with the deformations of the oriented fluid. There are three basic deformations of the director, slay, twist and bend, each of them having a specific elastic constant **K**.[20]

The free energy, **F**, associated with these deformations, if they are small, is written as:

$$F = \frac{1}{2}K_1\,(\mathrm{div}\ n)^2 + \frac{1}{2}K_2\,(n\ \mathrm{curl}\ n)^2 + \frac{1}{2}K_3\,(n \times \mathrm{curl}\ n)^2 \qquad (1)$$

where $\mathbf{K_1}$, $\mathbf{K_2}$ and $\mathbf{K_3}$ are the elastic constants of splay, twist, and bend deformations. **n** is the director and **curl** is the rotational operator. When a shear is deforming the equilibrium state of the director organisation, it creates an elastic contribution through additional defects or distortions, which will re-arrange towards the lowest energy state, generating an elastic recovery, as shown for example by Vermant *et al.*[21] The magnitude of the recovery will depend on the overall director organisation, its distortion and on the values of the elastic constants.

Two incompatible fluids will also show an elastic behaviour linked to their interfacial tension. When a fluid **A** is embedded into a matrix fluid **B**, the fluids being incompatible, the stable morphology is a sphere minimizing the interfacial area. When submitted to a stress, two phenomena are at stake, the stress, which tends to deform the drop, and the interfacial stress, which tries to minimize the interfacial area by resisting to this drop deformation. The capillary number **Ca**, the ratio of the shear stress and the interfacial stress as defined by Taylor,[22] expresses this competition:

$$\mathbf{Ca} = \frac{\tau \mathbf{R}}{\mathbf{T}} \qquad (2)$$

where **R** is the radius of the drop, τ is the shear stress and **T** is the interfacial tension. During an increase of the shear rate, the shear stress is progressively taking the dominating role and the drop will elongate up to a critical value of **Ca**, called **Ca***,above which the drop will break up.[23] This increase of interfacial tension is generating an elastic force, which can be used for measuring the interfacial tension.[24]

Contrary to the two other cases, where the elastic forces depend on many parameters, which are not easy to control and model, here the situation is simpler since the amount of parameters is small and well defined. The use of the Palierne model allows to calculate the elastic recovery[25] as:

$$\gamma_{r,\infty} = \mathbf{Ca}\ \mathbf{f}(\mathbf{p},\Phi) \qquad (3)$$

where $\gamma_{r,\infty}$ is the ultimate recoverable strain after a steady shear was applied and stopped, **Ca** is the capillary number (Eq.2), **p** is the viscosity ratio and Φ is the volume fraction of droplets. The recoverable strain is directly proportional to the capillary number and is proportional to the volume fraction of drops, not to their size.

EXPERIMENTAL

Klucel™ hydroxypropylcellulose (HPC) was kindly given by Ashland Aqualon. For this study, a sample with M_w= 9.5×10^4 g/mol was selected. Aqueous solutions of different concentrations from 20% to 55% (w/w) were prepared by hand mixing water and HPC at room temperature. Solutions were left several days at rest to remove air bubbles, in particular for the most concentrated solutions. Various phase diagrams of optical evaluation of the isotropic-nematic concentration are available in literature.[26,27] The first isotropic phase appears around 45%w/w, with the fully nematic state being around 55-60% w/w. Between 45% and about 50%, there is a biphasic state with a coexistence of twisted nematic and isotropic phases. The situation under flow is slightly different. First, the long range cholesteric twisting is destroyed by a flow. Second, the phase diagram is changed, the flow helping to move the biphasic region to slightly lower concentrations.[28,29]

Wacker® AK 50 with a dynamic viscosity of 50 mPa·s was used as silicone fluid.

Rheological measurements for HPC solutions were performed at 25°C on a Bohlin Gemini rheometer equipped with plate-plate geometry (diameter of 50 mm) and a Peltier temperature control system.

RESULTS AND DISCUSSION

Contribution of chain elasticity to shear elastic recovery

Creep and recovery tests allow distinguishing among solid, liquid and viscoelastic materials. During creep experiments, the applied shear stress, τ_o, is the controlled variable, and the resulting deformation, $\gamma(t)$, is measured. Generally, this is a nonlinear property depending on the applied stress, τ_o. When the profile of $\gamma(t)$ becomes linear, the fluid has reached a stationary flow condition. After the imposed τ_o is removed, the recovery starts and it permits the description of the time-variation of the deformation due to elastic contributions. Fig. 1 shows the creep-recovery curves obtained for an isotropic 45% HPC solution in water at 25°C after imposing deferent levels of stresses. During the creep, when a constant shear stress is applied, an increase of deformation in time is observed. The steady state situation, i.e. when the deformation is linearly increasing with time, is in the order of a few tenths of a deformation unit. For example, for an applied stress of 50 Pa, the linear regime starts after about 100 s, at a deformation of about 0.03 deformation units. When the stress is removed, the deformation is recovered first as a very fast process and then the delayed deformation is recovered progressively. The kinetics of strain recovery depends on several parameters, such as how many chains have been put out of conformation equilibrium, their connectivity and the viscosity of the medium. What is of interest here is not the kinetics, but the ultimate recovery value attained after a certain stress level has been applied.

The total recovered (elastic) deformation (γ_R) for the isotropic HPC solutions is in the order of one tenth of a deformation unit. The recovered deformation increases with HPC concentration (Fig. 2). This is due to the increase of chain connectivity with concentration. The recovered deformation is also increasing with imposed shear stress. For each concentration, there is a downward bending of the curve, which expresses the fact that there is a limit of chain stretching for each stress.

Contribution of orientational defects to shear elastic recovery in liquid crystalline solution

As stated in the introduction, a nematic liquid crystalline phase has a specific elastic behaviour during deformation due the intrinsic constraint of orientation. Without taking particular measures, such fluids have a polydomain morphology,[16] which means that the director takes different orientations in space. This generates regions where, locally, orthogonal orientations could be present. Particular orientational defects will be generated in order to minimize the free energy of the nematic fluid at these particular regions where difference director orientations meet. These defects were described earlier.[20,30] Upon deformation, most of these defects persist, generating even more distortions, which are then relaxed upon cessation of flow. This description is also valid for twisted nematics (or cholesterics), which is the case of HPC solutions above a concentration of 50%, since the long range cholesteric ordering is destroyed by the flow. Fig. 3 presents the deformation versus time obtained in creep-recovery tests for an anisotropic aqueous solution of HPC with the concentration of 55% HPC. The elastic deformations are very high if we compare with those shown in Fig. 1, and for better clarity we have shown the complete creep–recovery curves for two values of τ_o: 20 Pa and 50 Pa applied during creep and only the recovery part obtained after a creep at 100 Pa.

As in the case of isotropic solutions, there is an increase of deformation upon imposing a stress with a transient region before reaching a linear regime. For an applied stress of 50 Pa, the linear regime starts at a time of 30 seconds, for a deformation of 0.75 units, for the 55% solution (Fig. 3). If we compare to the isotropic state (Fig. 1), this is 57 times larger.

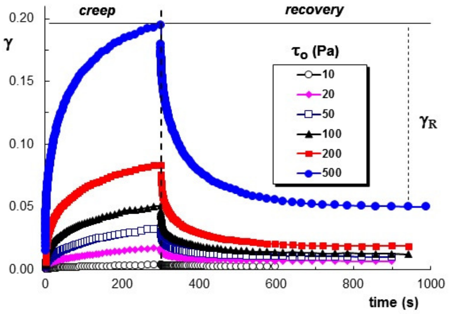

Figure 1: Deformation, γ, as a function of time, showing the creep and recovery curves obtained when applying different magnitudes of shear stress, τ_o, to an isotropic aqueous solution of HPC ($M_w = 9.5x10^4$) of 45% concentration (w/w) at 25 °C. Applied stress: 10, 20, 50, 100, 200 and 500 Pa;γ_R is the total recovered (elastic) deformation, here illustrated for an applied stress of 500 Pa

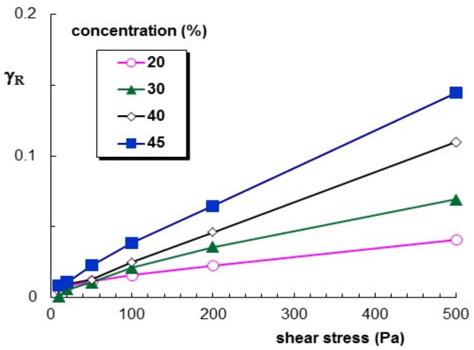

Figure 2: Elastic recovery as a function of applied shear stress during creep test for isotropic HPC solutions of different concentrations in water at 25 °C

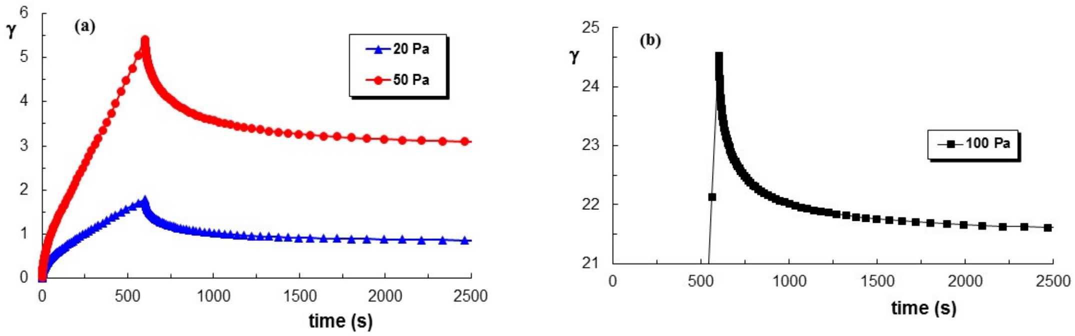

Figure 3: (a) Curves obtained in creep-recovery tests for a 55% HPC nematic aqueous solution. Stresses of 20 Pa or 50 Pa were applied during creep; (b) Stress of 100 Pa was applied during creep. For better clarity, only the recovery part of the curve is shown

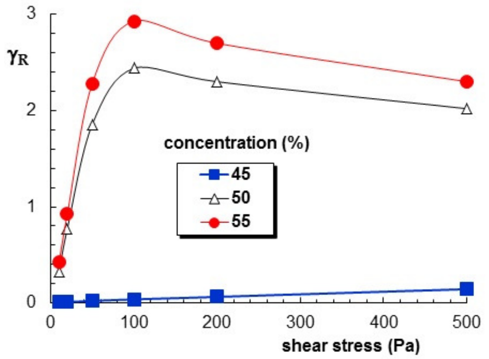

Figure 4: Elastic recovery as a function of applied shear stress after cessation of flow for two nematic HPC solutions (50% and 55% concentration). The data for the isotropic 45% HPC solutions are plotted for the sake of comparison

This is not due to viscosity reasons, the viscosities of the two solutions being in the same order of magnitude.[3] This is due to the need of re-arranging the defect structure, involving long range interactions and movements of chains over several mm.

Fig. 4 shows the recoverable strain γ_R values as a function of the applied shear stress. As already said, the values are more than ten times higher than those for an isotropic solution where only chain deformation occurs. An interesting feature is that the recoverable strain first strongly increases with stress, and then decreases. The increase is linked to the higher and higher defect network distortion when stress is increased, generating larger strain recovery. When the stress is above a certain value, here around 100 Pa, the flow is such that the director orients strongly in the flow direction, and defects start to annihilate. In addition, a particular transient texture will take place during relaxation, called banded texture,[2] leading to minimizing the energy of the system. This causes the recoverable elasticity to decrease at high imposed shear stresses.

Contribution of interfacial tension to shear elastic recovery

The system studied here is composed of isotropic drops of HPC 30% in poly(dimethylsiloxane). The value of the interfacial tension is 12.2 m.Nm^{-1}.[31] Upon shear, the drops of HPC solution will deform and eventually break up if the flow is strong enough. Two different cases are shown in Figs. 5 and 6 in order to illustrate the effect of drop deformation. In the first case (Fig. 5), the stress is low and the amount of imposed deformation is also low. Drops highly deform without breaking. Upon cessation of flow, they relax to a spherical shape, with a recoverable strain much higher than the one of the pure HPC solution at the same stresses. At 100 Pa, the pure solution has a recoverable strain of 0.018 units (compared to 0.07 units for the drops at 100 Pa) and 0.03 units (compared to 0.13 units for the drops) at 200 Pa. In the second case (Fig. 6), the stress is high (1000 Pa) and the amount of deformation is also large. The drops of HPC solution break down into smaller drops, which are much less deformable. The interfacial tension plays a smaller role during relaxation than in the previous case after cessation of flow. Since the chains are constrained into drops, they do not elongate much. The result is that the recoverable strain (0.03 units) is smaller than in the case of the pure HPC solution (0.057 units). This is possible because the flow inside the drop is much less severe than the flow in a single fluid.

A quantitative evaluation of different contributions of elastic recovery for HPC solutions in water and for drops of 30% HPC aqueous solution in a silicone oil matrix is illustrated in Fig. 7.

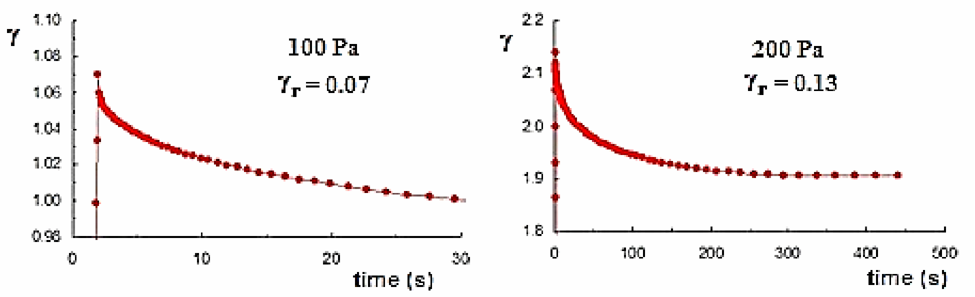

Figure 5: Recovery curve for drops of HPC 30% aqueous solution in a silicone oil matrix, after a creep at an imposed stress of 100 Pa with a deformation of 1 unit (left hand graph) and an imposed stress of 200Pa with a deformation of 2 units (right hand graph)

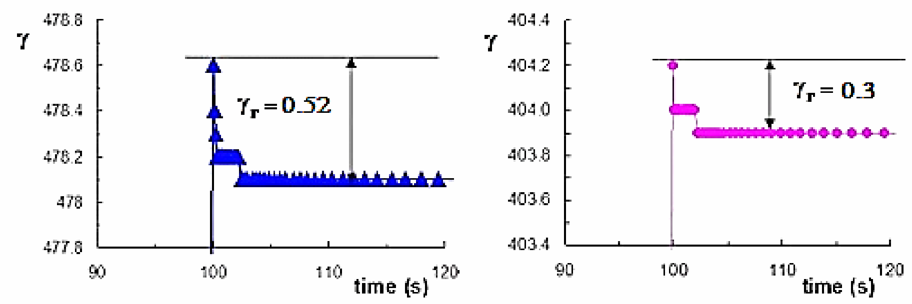

Figure 6: Recovery curve for 30% HPC (left hand graph) in water and (right hand graph) drops of HPC aqueous solution in a silicone oil matrix, after a creep at 1000 Pa for 100 s

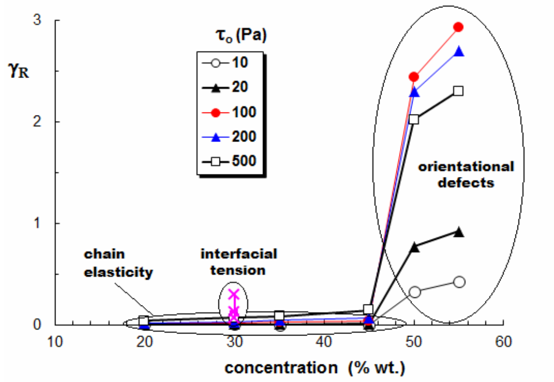

Figure 7: A quantitative evaluation of different contributions of elastic recovery for HPC solutions in water: isotropic solutions up to 45% HPC, anisotropic solutions above 45% HPC and the interfacial tension contribution for drops of 30% HPC aqueous solution in a silicone oil matrix (×)

CONCLUSION

The recovery results obtained in this work are summarized in Fig. 7. It illustrates the fact that a wide range of cooperative phenomena, such as the ones occurring in liquid crystalline phases, have great effects when such materials are flowing, with magnitudes of stored energies much higher than those encountered for isotropic polymer fluids. This is due to the fact that this elastic recovery involves many chain contributions in a long spatial range, thus allowing very large distortions, much larger than the ones that can be obtained by chain conformation changes in weakly cooperative polymer solutions.

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