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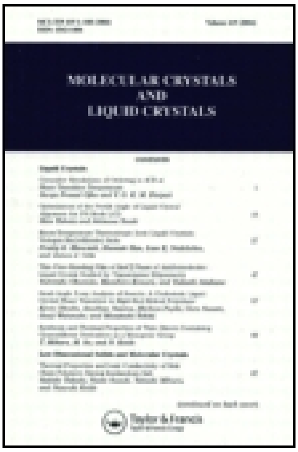

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Aging Effects on the Rheology of LC Solutions of Hydroxypropylcellulose

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AGING EFFECTS ON THE RHEOLOGY OF LC SOLUTIONS OF HYDROXYPROPYLCELLULOSE

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Abstract We apply the recently developed continuum theory of liquid crystalline polymers[1] to interpret the behavior of the shear viscosity $\eta(\dot{\gamma})$ and the first normal-stress difference $N_1(\dot{\gamma})$ measured for liquid crystalline solutions ($c=37\%$, $c>c^*$) of HPC (Aldrich, $M_w=100{,}000$) in acetic acid (AA) with different ages: 1 day, 1 month and 2 years. $\eta(\dot{\gamma})$ and $N_1(\dot{\gamma})$ were measured over four decades in $\dot{\gamma}$. $N_1(\dot{\gamma})$ is observed to change from positive to negative and again to positive, as the shear rate $\dot{\gamma}$ increases. $\eta(\dot{\gamma})$ shows a small newtonian plateau at low shear rates and a strong shear-thinning at higher values of $\dot{\gamma}$. The rate of decrease of $\eta(\dot{\gamma})$ in this region is not monotonous, as usual, but shows an "hesitation" similar to one previously observed in a different system[2]. The aging effect promotes a "depolymerization"[3] of HPC. This, in turn, should have a strong influence on the behavior of $N_1(\dot{\gamma})$ and $\eta(\dot{\gamma})$ which is indeed observed[4]. All these observations can be rationalized within the framework of the theory[1].

INTRODUCTION

Liquid crystalline (LC) behavior of hydroxypropylcellulose (HPC) in various solvents is a well known phenomenon[5-7]. In this work we describe the aging effects on the rheological properties of the solutions of HPC in acetic acid (AA), which are anisotropic (chiral nematic) above the critical concentration $c^*=30\%$ of HPC. The experimental behavior observed is analyzed in terms of the continuum theory for polymer liquid crystals recently proposed by Martins[1]. The effects of shear rate[8], concentration[8] and polymer molecular weight[4] on the rheological behavior of LC solutions of this system have been reported before.

It is well known that, in certain conditions, polymer degradation can occur with time. This effect is particularly strong in biodegradable polymers, which is the case of HPC. The effect of degradation on thermotropic HPC esters has been reported by Rusig et al.[3], who suggested that a "depolymerization" may arise as a consequence of aging the samples. The term "depolymerization" is used to describe the scission of polymeric chains, which corresponds to a decrease in the average molecular weight of the polymer.

THEORY

For nematic polymers in steady shear flow with constant shear rate $\dot{\gamma}$, with the director lying in the shear plane, Martins[1] derived the following expressions for the viscosity, $\eta(\dot{\gamma})$, the first normal-stress difference, $N_1(\dot{\gamma})$, and the second normal-stress difference, $N_2(\dot{\gamma})$, as functions of the shear rate:

$$\eta(\dot{\gamma}) = \eta_0 \exp(-\tau_0 \dot{\gamma}) + [a_0 (\tau \dot{\gamma})^2 + b_0 \tau \dot{\gamma} + c_0] \cdot [1 + (\rho \dot{\gamma})^2]^{-1} \tag{1}$$

$$N_1(\dot{\gamma}) = \sigma_{11} - \sigma_{22} = N_{10} + \dot{\gamma}[a_1(\tau\dot{\gamma})^2 + b_1\tau\dot{\gamma} + c_1] \cdot [1 + (1-\epsilon^2)\tau^2\dot{\gamma}^2]^{-1} \tag{2a}$$

$$= N_{10} + [a_1\tau^2 \dot{\gamma}(\dot{\gamma}-r_1)(\dot{\gamma}-s_1)] \cdot [1+(\rho\dot{\gamma})^2]^{-1} \tag{2b}$$

$$N_2(\dot{\gamma}) = \sigma_{22} - \sigma_{33} = N_{20} - 1/2(1-\epsilon)[N_1(\dot{\gamma}) - N_{10}] + \beta\dot{\gamma} \tag{3}$$

where a_i, b_i, c_i ($i = 0,1$) and β are known functions[1] of the "Leslie's viscosity coefficients" α_i[10], N_{10} and N_{20} represent Ericksen stresses that may exist at $\dot{\gamma} = 0$, τ is the relaxation time of the polymer memory function, τ_0 is related to texture relaxation modes, ϵ ($-1 \le \epsilon \le 1$) is a measure of the non-affine character of the motion and $\rho^2 = (1-\epsilon^2)\tau^2$.

EXPERIMENTAL

Three samples with different ages: 1 day, 1 month and 2 years, were analyzed. These samples were obtained from the same mother solution with concentration c = 37% of HPC (Aldrich, $M_w = 100{,}000$) in AA.

Measurements of the viscosity $\eta(\dot{\gamma})$ and the first normal-stress difference $N_1(\dot{\gamma})$ in function of shear stress, were carried out in a Instron 3250 cone and plate rheometer. The rheological device was equipped with cone and plate of radius 2 cm, and cone angle of 0.042 rad (low enough to ensure a pure shear flow). $\eta(\dot{\gamma})$ and $N_1(\dot{\gamma})$ were measured over four decades in $\dot{\gamma}$, between 0.1 - 5000 s^{-1}. The experiments were performed at room temperature. The second normal-stress difference $N_2(\dot{\gamma})$, although useful for a better flow characterization, could not be measured with our experimental setup.

RESULTS AND DISCUSSION

Expressions (1) and (2b) for the shear viscosity $\eta(\dot{\gamma})$ and first normal-stress difference $N_1(\dot{\gamma})$, were computer fitted to the experimental data by using the MINUIT routine[9]. The results obtained are displayed in Figs. 1 and 2, respectively. For the sake of clarity, we only represent the experimental data together with the corresponding theoretical (best fits) curves for the sample aged 1 month; the quality of the fits for which data is not shown is similar to this.

The most important parameters obtained directly from the fits are shown in TABLE I.

An "hesitation"[2] of $\eta(\dot{\gamma})$ in the shear-thinning region and a double sign inversion of $N_1(\dot{\gamma})$ can be observed for all samples, and the influence of aging on these peculiar phenomena is very clear. From Fig. 1, it can be seen that, when compared to the fresh sample (aged 1 day), the sample aged 2 years shows a strong decrease in the viscosity at low values of $\dot{\gamma}$. In Fig. 2, we observe for this sample a displacement of the $N_1(\dot{\gamma})$ curve to higher $\dot{\gamma}$ values. Both behaviors, of $\eta(\dot{\gamma})$ and $N_1(\dot{\gamma})$, observed

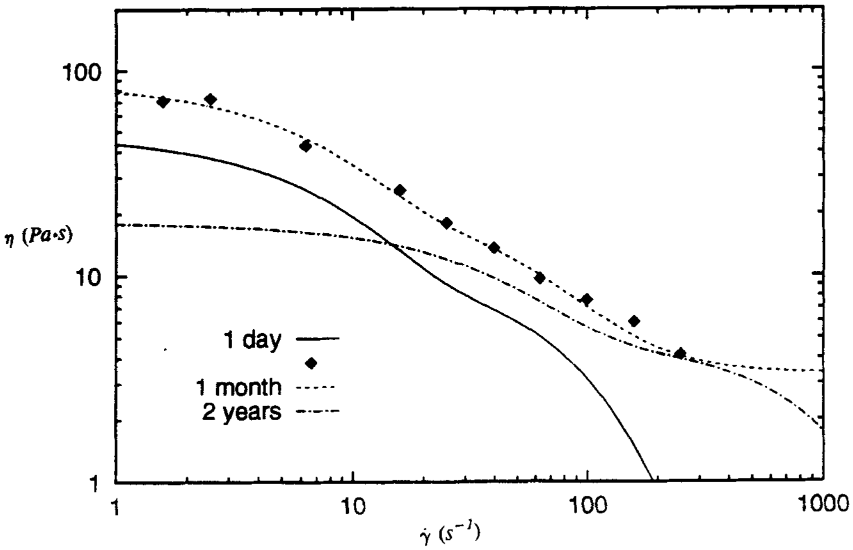

FIGURE 1 Shear viscosity vs shear rate, for samples (37% HPC/AA) with different ages: 1 day, 1 month and 2 years. Lines: theory[1], points: experimental data for the sample aged 1 month.

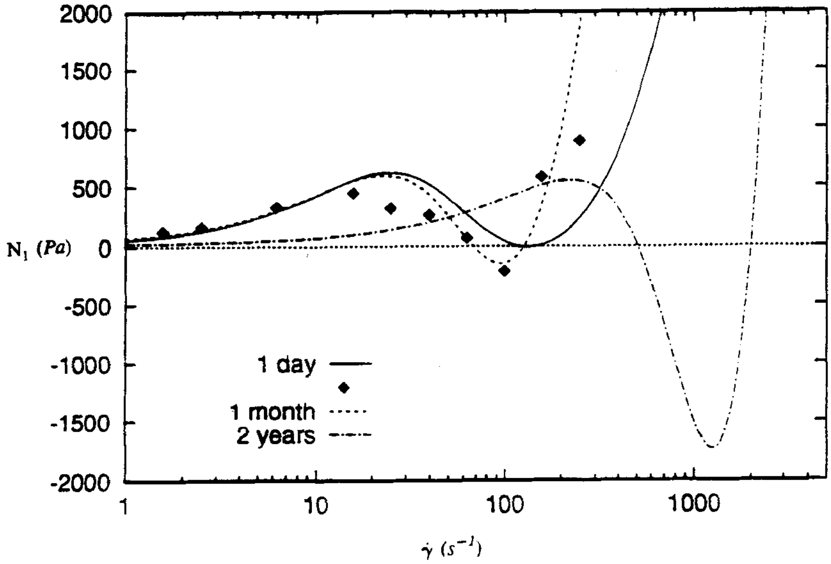

FIGURE 2 First normal-stress difference vs shear rate, for samples (37% HPC/AA) with different ages: 1 day, 1 month and 2 years. Lines: theory[1], points: experimental data for the sample aged 1 month.

for the 2 years sample, can be related to a decrease in the polymer molecular weight, which induce a decrease in the characteristic relaxation times τ and τ_0 and in the apparent "zero-shear" viscosity, (η_0+c_0). The influence of polymer molecular weight has been studied before for fresh samples of the same HPC/AA system and identical variations in the curves $\eta(\dot{\gamma})$ and $N_1(\dot{\gamma})$ were observed[4].

TABLE I Most important fitting parameters of $\eta(\dot{\gamma})$ and $N_1(\dot{\gamma})$ for samples (37% HPC/AA) with different ages: 1 day, 1 month and 2 years, (SI units).

Parameter	1 day	1 month	2 years
η_0+c_0	48.54	88.01	18.30
τ_0	0.13	0.14	2.5×10^{-2}
τ	9.9×10^{-3}	3.1×10^{-2}	2.6×10^{-3}

The parameters τ_0 and τ are strongly related with the "slope" of $\eta(\dot{\gamma})$ curve. τ_0 controls the beginning of the shear-thinning region and how rapidly $\eta(\dot{\gamma})$ decreases in the lower part of this region. τ influences the "hesitation" observed in the shear-thinning region. With a decrease of τ_0 and τ, the effects related with them are displaced to higher $\dot{\gamma}$ values. For this reason, the 2 years $\eta(\dot{\gamma})$ curve apparently does not decrease so rapidly (within the range of $\dot{\gamma}$ probed), when compared with the other ones, and crosses the 1 day curve (see Fig.1).

The displacement of the roots of $N_1(\dot{\gamma})$ curves with aging, first to lower $\dot{\gamma}$ values (in the 1 month curve) and after to higher $\dot{\gamma}$ values, is inversely related with τ. The greatest difference is observed between the 1 month and the 2 years samples, which is assigned to a stronger decrease in τ in this period. In fact, the mid point between the non-zero roots of the cubic polynomial in the numerator of the second term in the r.h.s. of expression (2a) is situated at $\dot{\gamma}=-b_1/2a_1\tau$, which justifies[4,8] the observed displacement of the roots of N_1 with τ.

The increase of the parameters τ, τ_0 and (η_0+c_0) observed from 1 day to 1 month, can be related to the chemical modification of the lateral substituents of the

HPC chains, probably due to the reaction between the esther groups of the AA and free hydroxyl groups of HPC. The substitution of the hydrogen by an esther group *increases* the polymer molecular weight, but when virtually all the free-OH groups in the HPC chain have reacted, the dominant effect of the interaction of the acid with the polymer may be a different one, namely, an hydrolysis of the HPC chains, which causes their scission and therefore a *decrease* of the average polymer weight. This explains the opposite behavior observed in the $\eta(\dot{\gamma})$ and $N_1(\dot{\gamma})$ curves of the 1 month sample as compared to the 2 years sample.

One can estimate the value of the polymer molecular weight for the 2 years sample by comparing the value of τ obtained in this case with the results obtained previously[4] for two different samples of HPC with molecular weights $M_w=100{,}000$ and $M_w=60{,}000$ (Klucel L and E, respectively). Assuming that the variations of τ and M_w with aging are proportional, the value obtained for the polymer molecular weight of the 2 years sample is $M_w \approx 27{,}000$, which seems to be in reasonable agreement with the above interpretation. This value may appear to be somewhat inaccurate, however, because the samples compared show some differences in their rheological behavior (the samples were from different origins, namely Aldrich and Klucel, and probably have different mass distributions).

CONCLUSION

The foregoing analysis of the experimental data in the framework of the continuum theory proposed by Martins[1] suggests that the main effects of aging of the HPC/AA system can be accounted for by variations in the viscoelastic parameters of the theory, in particular τ, τ_0 and (η_0+c_0) (see TABLE I). The variation of τ is assumed to correspond to a variation in the average polymer molecular weight, which in turn we explain as an effect of the reaction of the solvent (acid) with the polymer.

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