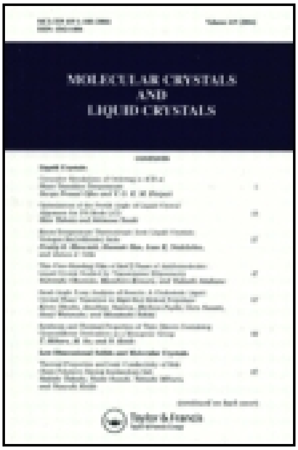

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RHEOLOGICAL PROPERTIES OF LYOTROPIC SOLUTIONS OF ACETOXYPROPYLCELLULOSE IN DIMETHYLACETAMIDE. A COMPARISION WITH THE THERMOTROPIC CASE

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RHEOLOGICAL PROPERTIES OF LYOTROPIC SOLUTIONS OF ACETOXYPROPYLCELLULOSE IN DIMETHYLACETAMIDE. A COMPARISION WITH THE THERMOTROPIC CASE

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The rheological properties of a thermotropic acetoxypropylcellulose (APC) were already described in previous works [1,2]. In this work we present the rheological properties, viscosity, η, and first normal stress difference, N_1, of lyotropic solutions of APC in dimethylacetamide (DMAc).

The flow curve of the lyotropic solution presents the typical behavior for this type of system (Onogi and Asada Curve) [3] however, contrary to what happens with that other lyotropic system [4–7], the APC/DMAc system presents a continuous increase of N_1 in function of the shear rate, which we attribute to the fact that APC has higher flexibility than the other liquid crystalline polymers studied so far—namely hydroxypropylcellulose and poly-benzyl-L-glutamate—that present a negative N_1 region, as well as a low molecular weight.

We will also present some remarks concerning rheo-optical studies preformed with APC/DMAc, by comparison with previous studies on thermotropic APC [8,9].

Keywords: viscosity; first normal stress difference; lyotropic solutions; thermotropic systems

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INTRODUCTION

The rheological behavior of liquid crystalline polymers, in the melt (thermotropics) or in solution (lyotropics), has been the aim of many studies due to their physical properties and technological importance, namely the high modulus fibers obtained by the extrusion of lyotropic systems and the high performance matrices (exceptional mechanical properties) processed from these polymers in the melt.

A considerable part of the work performed with these materials regards the study of the viscosity (η) and the first normal stress difference (N_1), in function of the shear rate ($\dot{\gamma}$) for lyotropic [4–7,10–13] and thermotropic systems [9,14–21], and the explanation for the observed behavior, which is much different from the that observed in the flexible polymers, in what concerns, for instance, the appearance of a three region flow curve (Onogi and Asada curve [3]) and the existence of a negative region of N_1(s).

The theoretical explanation for this type of phenomena as been one of the aspects of higher interest in the scientific community. Marrucci and Maffetone [22] proposed an explanation based on the molecular theory of Doi [23] for the existence of negative values of N_1, a theory that was later generalized (with a 3D treatment instead of 2D initially considered by Marrucci and Maffetone) by Larson [24] and Larson and Öttinger [25]. Developments of the molecular theory are still underway [26–28], taking into account particular aspects like orientation distorsions [27] or particular systems such as the shear aligned thermotropic one [28]. Continuum theories were also proposed, as the one presented by Farhoudi and Rey [29] and the one proposed by Martins [30] that includes modifications to the Leslie-Eriksen [31] theory, which was developed for low molecular weight liquid crystals and takes into account the viscoelasticity present in the liquid crystalline polymers.

Other interesting phenomena that have been systematically studied in these type of systems (both lyotropic and thermotropic), and that are known as *band texture*, concern the appearance of bands perpendicular to the shear direction, during relaxation and after cessation of shear [7c,8,9,12,32–36]. The bands are due to a periodic orientation fluctuation of the director and their appearance is generally regarded as the preferred mechanism for releasing the elastic energy, which has been stored in the material, during shear.

The study of the influence of factors like shear history, polymer molecular weight, solution concentration, temperature, etc., on the formation and relaxation of the band texture, as well as the explanation for the observed phenomena, has been the aim of several research works over the last two decades. A full review of the literature concerning this subject is given in Harrison and Navard [36].

The phenomena mentioned above, namely the appearance of negative values of N_1 in a certain shear rate range, have been observed in most of the studied lyotropic systems [4–7,10–12) rising the hypothesis of being a universal phenomena in this type of system. For the thermotropic systems, the appearance of a negative region of N_1 has been reported [14,16], and brought a lot of discussion [17–19], but the most general opinion is that this region does not exist in these systems.

In our previous works it was showed that the thermotropic APC do not present, in the experimentally probed shear rate range, and for the studied temperatures (120–140°C), any negative N_1 region. However, it was observed that for high shear rates an inflection occurred, an inflection that has previously been described for high concentrations of HPC/acetic acid [6b] and HPC/m-cresol [5b,5c]. For this reason the thermotropic system was interpreted as the limit for the high concentrations, for which the existence of a negative N_1 region no longer exists.

Profiting from the fact that APC presents both lyotropic (even at very high concentrations) and thermotropic phases, we have studied a large concentration range of APC/DMAc solutions in order to search for the existence, or not, of negative N_1(s) in this system. These results are now presented.

EXPERIMENTAL PROCEDURE

The synthesis and characterization of APC has been described already [1]. In this study an APC sample with an average molecular weight of 51300 Dalton and with an isotropization temperature of 170°C was used. The low average molecular weight obtained when compared with the starting HPC (60000 Dalton) can be explained by the excess of acetyl chloride used in the reaction, which produced a high percentage of chloridric acid responsible for the observed depolymerization.

The critical concentration for the lyotropic system APC/DMAc was determined by optical microscopy with polarized light, and it is $c^* \approx 60$ wt%.

For the rheological measurements, seven concentrations of APC/DMAc were prepared: 51.7, 62.0, 67.7, 75.6, 80.2, and 89.8 wt%, the first one in the isotropic state and the others in the liquid crystalline domain.

The rheological properties for the six lowest concentrations were determined at 25°C and for the two higher concentrations, along with the thermotropic APC, at 80°C. The rheological measurements were carried out on a rotational rheometer (Rheometrics Scientific RMS 800) using a cone and plate geometry, with radius of 12.5 mm and a cone angle of 0.1 rad. The measurements were performed in the steady state, using the "step shear rate" mode, at shear rates ranging from 1 to 1000 s^{-1} for the measurements at 25°C and at shear rates ranging from 0.2 to 60 s^{-1}, for the measurements at 80°C, under nitrogen atmosphere. The zero values of the normal force and torque were set, for each testing temperature, before introducing the sample. After loading, the sample was squeezed between the cone and plate to give a 46 μm gap and the excess sample was removed. The normal force was allowed to decrease back to its true zero value before the test took place. The measurements at 80°C implied the use of an antievaporation system. Thirty minutes was typically allowed for thermal equilibration for measurements performed at 80°C, higher than the ones used for measurements at 25°C.

The measurements were performed over at least two different samples for each solution in order to assure the reproducibility of the results. The results presented are the ones obtained in the first measurement, on a virgin sample.

Rheo-optical studies were also performed with the solutions of concentrations between 51.7 and 80.2 wt%, at 25°C, using a rotational rheometer, Instron 3250, with cone and plate geometry (both in polished quartz), to which was associated a Wild-Leitz microscope, with 10 × magnification lens and a video camera. This system has been described already in detail [37].

RESULTS AND DISCUSSION

Figures 1 and 2 present the experimental data on the viscosity and first normal stress differences, respectively, for the APC/DMAc solutions at 25°C, while Figures 3 and 4 present the experimental results of the measurements of the viscosity and the first normal stress difference for two concentrated solutions of APC/DMAc (80.2 and 89.8 wt%) and for thermotropic APC at 80°C.

Figure 1 shows that the isotropic solution exhibits a behavior typically found for flexible polymers with a quasi-newtonian plateau at low and intermediate shear rates, followed by a shear-thinning region for the higher shear rates.

Figures 1 and 3 show that, for the thermotropic APC at 80°C, as well as for the higher concentrations (75.6 and 80.2 wt%) at 25°C, the viscosity curve presents a three region flow curve, as predicted by Onogi and Asada [3] for liquid crystalline solutions. However, for the concentrated solutions of APC/DMAc at 80°C, as well as for the less concentrated solutions of APC/DMAc at 25°C, and within the experimentally accessible shear rates, two or

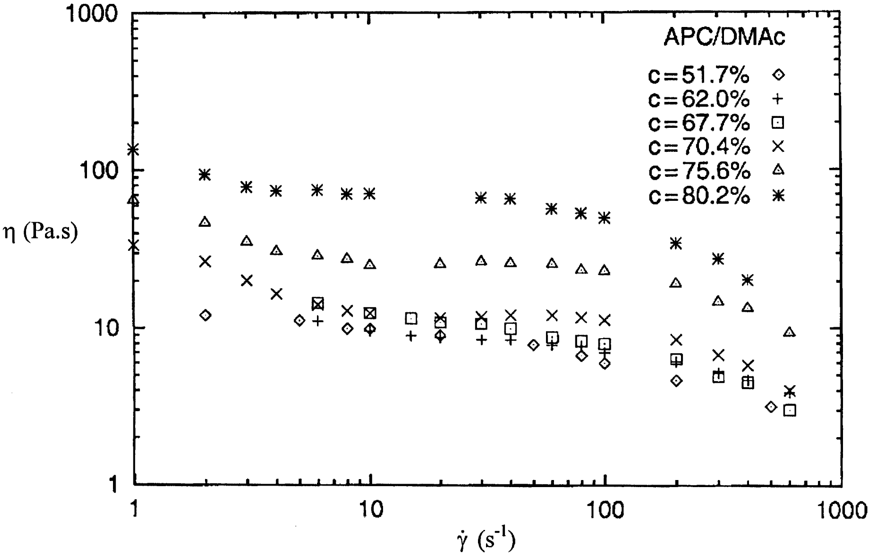

FIGURE 1 Viscosity versus shear rate for the APC/DMAc solutions, at 25°C.

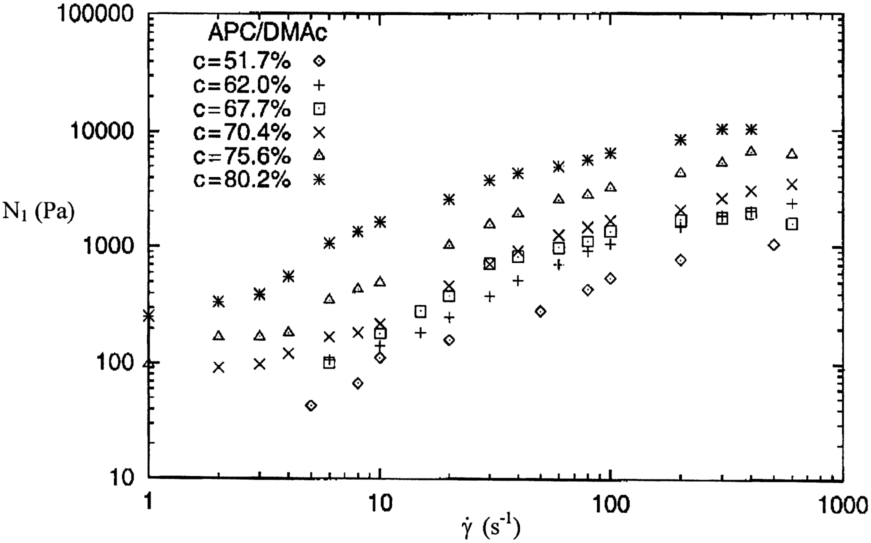

FIGURE 2 First normal stress difference versus shear rate for the APC/DMAc solutions at 25°C.

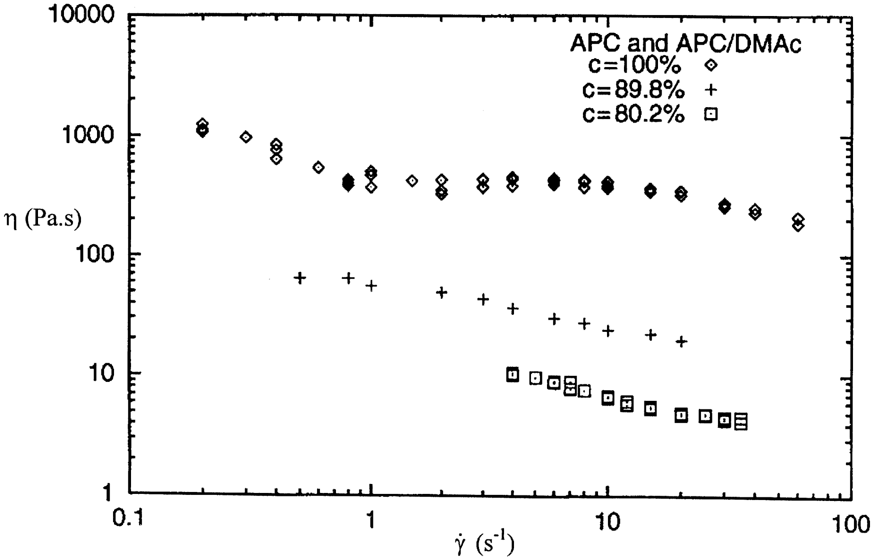

FIGURE 3 Viscosity versus shear rate for APC and APC/DMAc with concentrations of 80.2 and 89.8 wt% at 80°C.

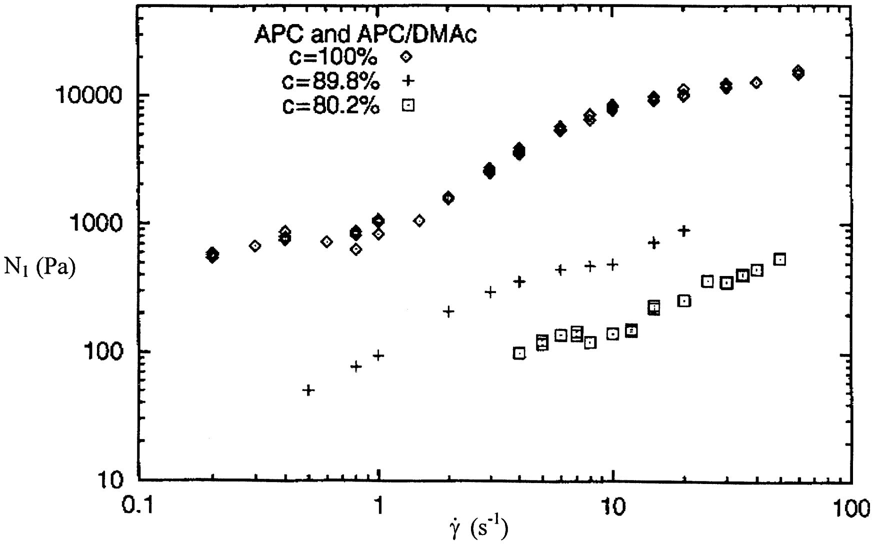

FIGURE 4 First normal stress difference versus shear rate for APC and APC/DMAc with concentrations of 80.2 and 89.8 wt% at 80°C.

even one region was observed. This observation is explained by the fact that, for a decreasing of the concentration, the shear rate corresponding to the transitions between different regions shifts to higher shear rates, as predicted by Martin's continuous theory [30] and experimentally proved [6a, 6b, 38]. It is important to point out that the decreasing of the value of $\dot{\gamma}$ at which the transitions occurs, with the increasing of the concentration, is only observed with solutions which concentration lies in the rising branch (anisotropic domain) of the η(c) curve, as it is in our case. For the solutions for which concentration lies in the descending branch the opposite is observed, as it is in the case, for instance, for the PBLG/m-cresol system (concentrations of 12.5 and 14 wt%) [7b].

Figures 2 and 4 show that, at least within the shear rate range experimentally accessible, N_1 is always an increasing function of $\dot{\gamma}$, contrary to what happens with other well studied lyotropic systems, like HPC/H_2O [4a–4c], HPC/m-cresol [5a–5c], HPC/acetic acid [6a,6b] and PBLG/m-cresol [7a–7c], for which a negative region of N_1 is observed for intermediate shear rates.

This fact may be explained by the higher flexibility of this system in respect to the others. It is well known that PBLG behaves as rod-shaped macromolecules, while HPC behaves as semiflexible macromolecule, as APC does. Comparing HPC and APC, the flexibility of the former must be higher than the other due to intermolecular hydrogen bonding, at least for solutions prepared with the same solvent. The critical concentration of the system in this study is also an indication of the stiffness of the systems [39]. In fact, the critical concentration of HPC/DMAc is about 46 wt% [40] (nominal $\overline{M}_W = 93000$), while the critical concentration of APC/DMAc is, as already said, 60 wt%, which confirms the higher flexibility of our system when compared with HPC/DMAc. The critical concentration of PBLG/m-cresol is about 10 wt% [7a] (nominal $\overline{M}_W = 150000$) and of HPC/H_2O [40–42], HPC/AA [6a], and HPC/m-cresol [5a,5b,43] are about 40–45 wt% (nominal $\overline{M}_W = 60000–100000$), 30 wt% (nominal $\overline{M}_W = 100000$), and 22.5–25 wt% (determined $\overline{M}_W = 90000–185000$), respectively, which once again proves the higher flexibility of our system, even though we are comparing systems with different solvents (from the results of lyotropic HPC we conclude that the higher flexibility is obtained with DMAc, the solvent we used) and different molecular weights (the effect of molecular weight is not very pronounced, as observed above). We conclude that the system APC/DMAc is the most flexible among the different lyotropic systems studied so far, which may explain that the shear rates necessary for the attendance of negative N_1 values (if existing), are higher than in the other cases and higher than the ones experimentally probed. Note that the shear rates for which N_1 presents negative values seem to increase with the flexibility of the system in study (except for HPC/H_2O), as we can conclude when comparing the negative N_1 regions of different systems, at the same temperature (25°C): the shear rate range for which N_1 is negative, about 13–130 and 20–300 s^{-1} for 12.5 and 14% PBLG/m-cresol (determined $\overline{M}_W = 238000$), respectively [7b]; 45/50–120 s^{-1} for 45 wt% HPC/m-cresol (determined $\overline{M}_W =$ 90000 and 117000) [5c, 43], and 200–1800 and 63–2400 s^{-1} for 37% and 45% HPC/AA (nominal $\overline{M}_W = 60000$), respectively [6a]. For 50 wt% HPC/H_2O different shear rate ranges for which N_1 present negative values, have been found depending on molecular weight and author, namely 1–13 s^{-1} (nominal $\overline{M}_W = 100000$)[4a], 10–100 s^{-1} and 100–200 s^{-1} (nominal $\overline{M}_W = 100000$ and 60000, respectively) [4b]. Ernst and Navard [12] did not find any negative N_1 regions for shear rates up to 100 s^{-1}, even though N_1 starts decreasing at about 10 s^{-1}, for 50 wt% HPC/H_2O (nominal $\overline{M}_W = 100000$ and 60000). The differences found for HPC/H_2O may be attributed to different manufactures and/or grades of the polymer.

Another explanation for the expected higher shear rate range necessary for the appearance of negative N_1 values in our system is the low average molecular weight of the APC under study. As observed by Sigillo and Grizzuti for the system HPC/H_2O [4b], by Martins et al. with the system HPC/AA [6b, 38], and by Glesson et al. for the PBLG/m-cresol system [7c], the decreasing of the average molecular weight shifts $\dot{\gamma}$, for which the double sign inversion of the $N_1(\dot{\gamma})$ curve occurs, to higher shear rate values.

According to the theories of Larson [24] and Larson and Öttinger [25], at high shear rates the system reaches the steady state where the director keeps a constant orientation angle with the flow direction, an angle that depends on the system and on the imposed shear rate. Nevertheless, at low and intermediates shear rates the situation is much more complex, with the director suffering periodic or stationary behaviors depending on the initial conditions. One can distinguish three types of periodic solutions [24,25]. Two of them occur when the director initially lies in the shear plane (defined by the velocity field and the gradient of velocity field vectors) and are known as “tumbling” (at low shear rates) where the director describes periodically complete turns in the shear plane and “wagging” (for intermediates shear rates) where the director suffers an oscillating regime in the shear plane between two limiting angles. The third periodic solution, that occurs when the director is initially out of the shear plane, is known as “kayaking,” in which the oscillations occur out of the shear plane. The negative region of N_1 appears for shear rate values near the transition between the periodic situations and the steady state. These values are close to the ones where one can also observe the transition between the second and the third regions of the $\eta(\dot{\gamma})$ curve. According to this statement, the lyotropic system APC/DMAc seems to be of the nontumbling type. It is worthwhile to point out that, in our case, contrary to what

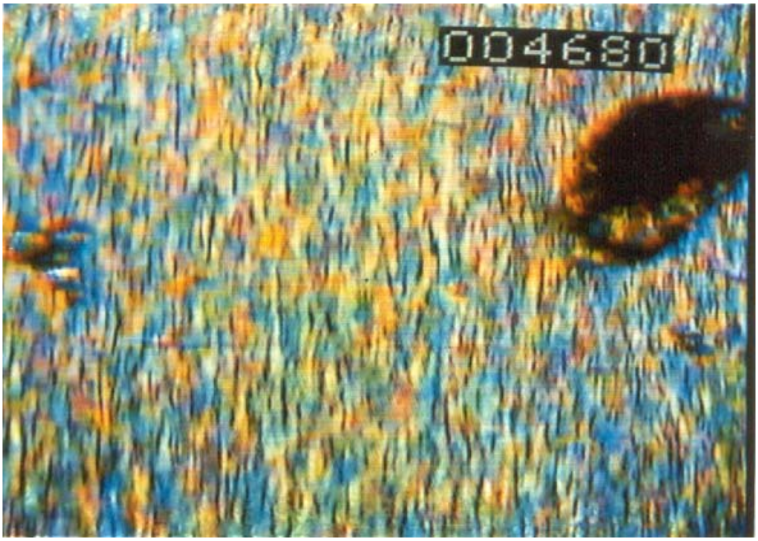

FIGURE 5 Typical band texture of APC systems. (See COLOR PLATE V)

happens with other anisotropic melt or any liquid crystalline high concentrated solutions (for which it is impossible to use N_1 to look for tumbling, since after loading the sample the normal force do not relax back to zero in a reasonable length of time before degradation takes place) [5c], our sample is stable enough, allowing for measurements during high periods of time, in particular allowing for complete relaxation of N_1 before the experiment takes place.

The rheo-optical observations performed with the lyotropic solutions during steady-state shear flow revealed textures very similar to the ones found for the thermotropic APC, with an average molecular weight of 88000 Dalton and at 120°C [8]. The major difference found is related with the relaxation after cessation of shearing. As is the case for the thermotropic APC, during relaxation a band texture appears (see Figure 5), but in this case this texture is quickly destroyed by a mechanism of "back flow" that does not occur in the thermotropic APC. However, the low times for the band texture of lyotropic APC/DMAc to disappear, during relaxation, are the usual times for lyotropic systems [12,32].

CONCLUSIONS

This work has allowed for the comparison between lyotropic and thermotropic APC, a polymer that presents mesophases in a wide range of concentrations, that goes from c* ≈ 60 wt% (for a molecular weight of 51300 Da) up to very high concentrations (c ≥ 90 wt%), as well as for the pure polymer. Concerning the viscosity curves, aside from the absolute values of the viscosity (for the same shear rates) that decrease with the dilution of the solution as expected, no significant differences are found in the behavior of the lyotropic solutions when compared with the thermotropic system.

In respect to the first normal stress difference, lyotropic and thermotropic APC also present the same type of behavior, with N_1 presenting always positive values, within the shear rate range experimentally accessible. The different behavior between lyotropic APC/DMAc solutions and other well known lyotropic systems [4a–4c,5a–5c,6a,6b,7a–7c] is attributed to the higher flexibility of APC when compared with other polymers like HPC or PBLG and it's low average molecular weight.

The rheo-optical studies performed with the lyotropic solutions of APC/DMAc, both during steady-state shear flow and after cessation of shear, show the same type of textures, including a band texture during relaxation presented by thermotropic APC. However, a major difference is the time that takes for the band texture to disappear during relaxation, which is very short (seconds) in the solutions and very high (several hours) in the thermotropic APC.

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