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Experimental Results on Electrorheology of Liquid Crystalline Polymer Solutions

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Abstract. The electrorheological (ER) effect is known as the enhancement of the apparent viscosity upon application of an external electric field. Suspensions of polarizable particles in non-conducting solvents are the most studied electrorheological fluids, however, liquid crystalline materials may also present ER effect as long as their dielectric anisotropy is positive. In the liquid crystalline state of a positive dielectric anisotropy, the application of the electric field makes the director align perpendicular to the flow direction, thus increasing the apparent viscosity.

In this work results of two liquid crystalline polymer solutions, acetoxypropylcellulose (APC) in dimethylacetamide (DMAc) and poly-γ-benzyl-L-glutamate (PBLG) in 1,4-dioxane, presenting opposite behavior upon application of the electric field, will be presented. APC/DMAc (negative dielectric anisotropy) presents a decrease of the apparent viscosity upon application of the electric field, as expected, while PBLG/1,4-dioxane (positive dielectric anisotropy) presents the opposite behavior. For this last solution we will present the shear flow curves for different electric fields in function of polymer molecular weight and solution concentration.

Keywords: Electrorheology, PBLG, Liquid crystalline polymers.
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INTRODUCTION

The large enhancement in the apparent viscosity observed in several fluids upon the application of an external electric field, first reported by Winslow[1], is known as electrorheological effect (ER).

This behaviour has been observed in different types of fluids. In suspensions of polarizable particles in insulating solvents, the most studied systems, the shear stress enhancement reaches more than 10 times its value without electric field, however these systems do not favor their technological applications due to particle sedimentation.

In homogeneous fluids like low molecular weight liquid crystals[2] or even solutions of flexible polymers with polar side groups, the ER effect also enhances the apparent viscosity several times, but never reaches 10 times its value. More significant enhancement have been reported for a thermotropic LC side-chain polymer[3] as well as for lyotropic polymers with rodlike molecules with high aspect ratio, namely solutions of PBLG/1,4-dioxane[3,4].

In this work further investigations have been carried out over the system PBLG/1,4-dioxane, taking into account the concentration and the molecular weight dependences. The results for a lyotropic system with semi-flexible molecules, namely APC/DMAc are also presented. These two systems present opposite responses in the ER behavior, since PBLG/1,4-dioxane shows an increase in the apparent viscosity upon application of the electric field, while in the APC/DMAc the apparent viscosity decreases under the same electric field conditions. This opposite response can be explained taking into account that PBLG has a positive dielectric anisotropy, while APC has negative dielectric anisotropy and positive dielectric anisotropy induces the orientation of the director in the perpendicular direction to the electric field, leading to an increase of the apparent viscosity.

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EXPERIMENTAL

Materials / Systems

Two lyotropic liquid crystalline polymer systems are studied in this work. One is the acetoxypropylcellulose (APC) (with molecular weight Mw=129000 g/mol, synthesized as described by Tseng et al.[6]), in solution with dimethylacetamide (DMAc), with a polymer concentration of 60 wt%. All chemicals were obtained from Sigma-Aldrich (min. purity 99,5%) . In the following this system will be referred to as APC/DMAc.

The second system is obtained from the poly-γ-benzyl-L-glutamate (PBLG) in solution with 1,4-dioxane, respectively from Sigma-Aldrich and Panreac (min. purity 99,5%). Two viscosimetric polymer molecular weights, Mw_{vis}, were considered in this study: 168000 g/mol and 117000 g/mol. From the highest, two solutions with polymer concentrations of 14 and 17 wt% were prepared, and from the lowest only a solution with 14 wt% was studied.

All the solutions present liquid crystalline properties at room temperature, which was confirmed by optical microscopy under crossed polarizers.

Electrorheology

The experiments were carried out in an Bohlin Gemini HR^{nano} rotational rheometer, equipped with an electrorheological cell. All the measurements were obtained with a parallel plate geometry, with 25 mm diameter. and a gap of 500 µm. In the case of PBLG/1,4-dioxane a temperature of 25 °C was used, while for APC/DMAc the temperature was set to 60 °C.

The flow curve $\eta(\dot{\gamma})$, under steady-state conditions, was obtained applying the following procedure: pre-shear of 1 s^{-1} during 120 s, followed by an equilibration time of 300 s, followed by a step shear rate increment procedure, ranging from 0.5 – 900 s^{-1} (for PBLG/1,4-dioxane) and from 0.1 – 900 s^{-1} (for APC/DMAc). The measurements were performed imposing a minimum of 200 deformation units for each shear rate in order to assure the steady state. In each essay the electric field was applied perpendicular to the flow direction, varying from 0 to 3 kV/mm.

The rheological behaviour under an electric field can be observed for the 60% APC/DMAc solution in FIGURE 1, and for the 14% PBLG/1,4-dioxane solution in FIGURE 2.

The influence, with and without electric field applied, of the polymer concentration for the system PBLG/1,4-dioxane (Mw_{vis} = 168000 g/mol) is presented in FIGURE 3, and of the polymer molecular weight dependence in FIGURE 4.

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RESULTS

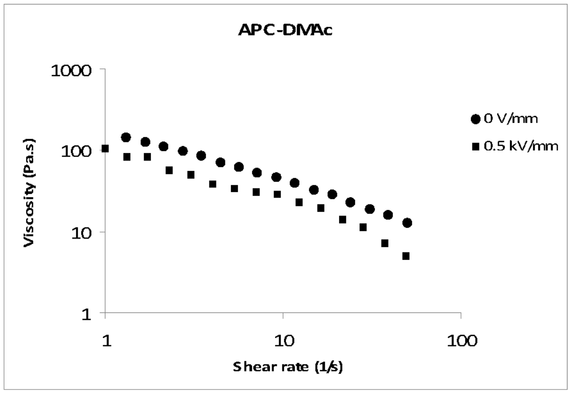

FIGURE 1. Flow curve for the solution of 60 wt% APC/DMAc, with and without the application of an electric field of 1 kV/mm, perpendicular to the flow direction.

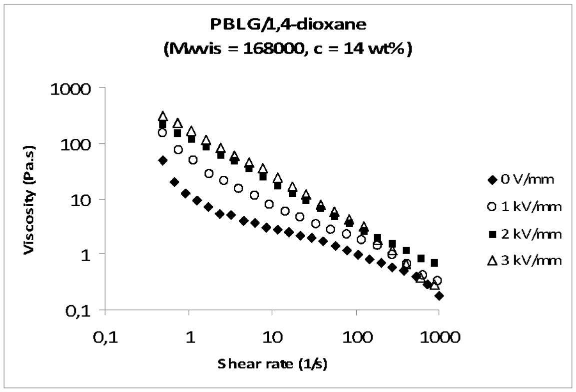

FIGURE 2. Flow curve for the solution of 14 wt% PBLG/1,4-dioxane(Mw_{vis} = 168000 g/mol), for different electric fields (0, 1, 2 and 3 kV/mm).

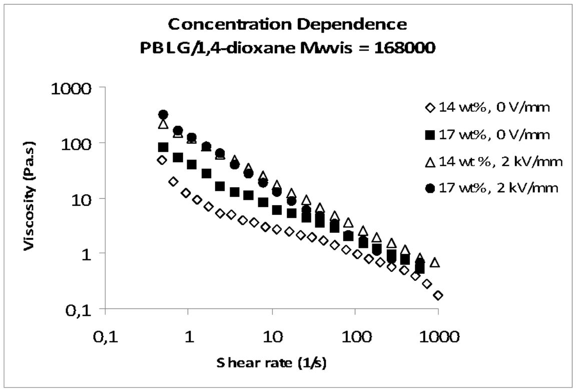

FIGURE 3. Flow curve for solutions of 14 and 17 wt % PBLG/1,4-dioxane (Mw_{vis} = 168000 g/mol), with and without the application of an electric field of 2 kV/mm.

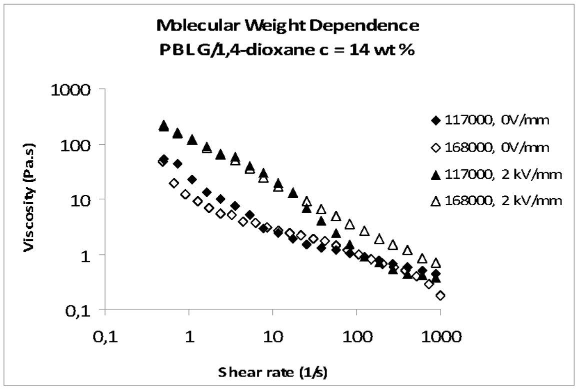

FIGURE 4. Flow curve for solutions of 14 wt% PBLG /1,4-dioxane, for two viscosimetric polymer molecular weights: 168000 and 117000 g/mol, with and without the application of an electric field of 2 kV/mm.

CONCLUSIONS

APC/DMAc, with a negative dielectric anisotropy does not present ER effect, while the PBLG/1,4-dioxane, with a positive dielectric anisotropy does, as expected.

For PBLG/1,4-dioxane a saturation of the shear viscosity seems to occur for electric fields higher than 2kV/mm. The concentration dependence is much more pronounced in zero than in non zero electric field, the pseudoplasticity being the probable cause for the observed behaviour. In fact, the application of the electric field seems to enhance the pseudoplasticity index, especially for the higher concentration. The shear viscosities for the two concentrations approach each other at low shear rates and there is a crossover of the two curves at intermediate shear rates.

A similar behaviour is observed for the molecular weight dependence, even though, in this case, the relaxation time may be the probable cause. In fact the lower molecular weight PBLG has a shorter relaxation time, which means that in the competition between the alignment due to the electric field and the flow field the latter is favoured for higher shear rates.

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