LYOTROPIC LIQUID CRYSTALLINE CELLULOSE DERIVATIVES IN BLENDS

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ABSTRACT

Cellulose and some of its derivatives can form liquid crystalline solutions in a variety of solvents. In this context, the present work investigates a series of blends obtained from 0/100, 25/75, 50/50, 75/25, 100/0 wt./wt cellulose acetate phthalate (CAP) / hydroxypropyl cellulose (HPC) in N,N-dimethylacetamide (DMAc). The flow behaviour of their mixed solutions was investigated by means of shear viscometry and oscillatory shear tests. The effect of composition, temperature and shear rate on the rheological functions reflects the orientation or mobility of the chain segments in the shear field. These studies contribute to the knowledge of specific interactions - which can modify liquid crystalline properties of cellulose derivatives, and to diversify their applications in electronic domain.

INTRODUCTION

A successful alternative for the development of new polymeric materials is blending of the already existing polymers, to obtain a balance among the desired properties exhibited by the individual components. Improvement of characterization techniques have led to understanding of mechanisms involved in polymers mixing, considering their fundamental interactions, and manner in which these interactions affect their final properties. It is well-known that the properties of polymer blends depend on the rheology of their solutions. When a component becomes an anisotropic fluid, it is expected that the anisotropic interfacial properties would greatly affect the blends properties. Polymer/liquid crystal polymer (LCP) blends have been intensively investigated as to their unique properties, such as those electrical, optical, mechanical properties. The self-aligning nature of LC is used for obtaining organic polymer thin-film transistors (OP-TFTs) in liquid crystal display devices.

CAP is a mixed ester of cellulose obtained trough phthaloylation of cellulose acetate. It is utilized in different domain such us pharmaceutical excipient, due to pH dependent solubility of aqueous medium.

NOMENCLATURE

CAP	[-]	Cellulose acetate phthalate
HPC	[-]	Hydroxypropyl cellulose
DMAc	[-]	N,N-dimethylacetamide
LCP	[-]	Liquid crystal polymer
OP-TFTs	[-]	Organic polymer thin-film transistors
GS	[-]	Degree of substitution
DSac	[-]	Acetylation degree
DSph	[-]	Phthaloylation degree
E_A	[KJ/mol]	Activation energy
E_{ass}	[KJ/mol]	Association energy
E_{dis}	[KJ/mol]	Dissociation energy

Special characters

η	[Pa · s]	Dynamic viscosity
$\dot{\gamma}$	[1/s]	Shear rate
σ	[Pa]	Shear stress
K	[Pa · s^n]	Consistency index
n	[-]	Flow index
η_0	[Pa · s]	Zero shear-rate viscosity
R	[J / mol · K]	Universal Gas Constant
T	[^{0}K]	Temperature
E	[J]	Energy
wt.	[%]	Gravimetric fraction

Cellulose acetate phthalate enteric coatings are resistant at gastric acid and are easily soluble in slightly alkaline environment of the intestine. PH-dependent solubility is mainly determined (among other properties of the mixed ester) of the degree of substitution (GS) namely average number of substituient groups linked to unit anhydroglucopiranose and molar fraction (acetyl and phtaloyl groups). These two structural characteristics of polymers are dependent on the synthesis conditions. Recently was analysed, in vitro, potential of this polymer to inhibit infections caused by several types of herpes virus such us Herpes Simplex type 1, and and other sexually transmitted diseases [1-4]. Also, CAP was utilised as enteric coating for films and pharmaceutical tablets, which confirms the safety of the human body.

On the other hand, in the crystalline state, the HPC molecules are present in a helical arrangement. The structure is not dependent on the solvent alone, but also on the concentration [5]. Fundamental research on the formation of banded textures in thin-film samples from lyotropic HPC solutions subjected to shear is important, due to the large number of physical interactions involved [6,7]. Moreover, the surface anisotropy of the mechanical and optical properties of the polymer films [8], together with their potential use as alignment layers for liquid crystal displays, make these systems particularly interesting and promising for new applications. Flow behaviour is the most thoroughly studied rheological property. Onogi and Asada [9] hypothesized the universal existence of three shear flow regimes to describe the viscosity of polymer liquid crystals: a shear thinning regime at low shear rates (Region I), a Newtonian plateau at intermediate shear rates (Region II), and another shear thinning regime at high shear rates (Region III). Region I, observed at low shear rates, shows shear thinning, exhibiting a yield stress, as in some plastic materials. This region is characterized by distortional elasticity associated with spatial variation in the director field (average local molecular orientation). Region II is a Newtonian plateau, reflecting a "dispersed polydomain" structure and Region III is a shear thinning zone, showing viscoelastic behaviour. In Regions I and II the flow is not strong enough to affect molecular orientation, while in Region III the flow field is very strong, so that the shear induces molecular orientation. Literature [9] shows that cellulose derivatives do not always cover the entire domain from Region I to Region III, because not every regime lies within the accessible shear rate range.

The present work investigates a series of blends obtained from CAP and HPC in N,N-dimethylacetamide at different mixing ratios and concentrations. The aim of the paper is to correlate the rheological behaviour of solution with specific interactions from the system which can modify liquid crystalline properties of cellulose derivatives and their applications in electronic domain.

EXPERIMENTAL

Cellulose acetate with a 1.93 a substitution degree was used for the synthesis of cellulose acetate phthalate. Cellulose acetate was phthaloylated with phthalic anhydride in acid acetic using anhydrous sodium acetate and triethylamine as basic catalysts [10]. The degrees of CA acetylation (DSac) and of CAP phthaloylation (DSph) were 1.73 and 0.7, respectively.

Hydroxypropyl cellulose (HPC) (LF, Klucel™) was purchased from Aqualon Company, Hopewell, Virginia, USA. According to product specifications, HPC LF has a molecular mass of approx. 100,000 g/mol and "moles of substitution" of 3.4.

Viscometric and oscillatory measurements for cellulose acetate phthalate/hydroxypropyl cellulose blends, in N,N-dimethylacetamide (DMAc) were obtained with a Bohlin Instrument, by the cone and plate measuring system; the cone had an angle of 4° and a diameter of 40 mm.
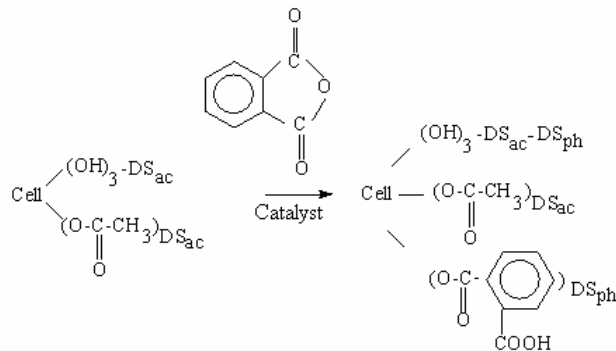

Figure 1 Obtaining of cellulose acetate phthalate from cellulose acetate with 1.93 substitution degree in presence of phthalic anhydride [10].

Shear viscosities were registered over the 0.07–1000 s^{-1} shear rate domain, at several temperatures (25–55 °C). During the oscillatory shear tests, the frequency was varied between 0.1–150 Hz, and a shear stress, σ, of 3 Pa was applied.

RESULTS AND DISCUSSIONS
Dynamic viscosity of CAP, HPC and CAP/HPC blend

The microstructure and polymer-solvent interactions of the lyotropic mesophases were derived from rheological studies. From this reason, present studies refers to the rheological investigation of CAP, HPC and their blends in N,N-dimethylacetamide, where appear anisotropic comportment in specific conditions on temperature, concentration and/or blend composition. Some studies have reported that the polymer structures, their mixing ratio and used solvent influence the interactions from systems and thus ordered domains in rheological behaviour.
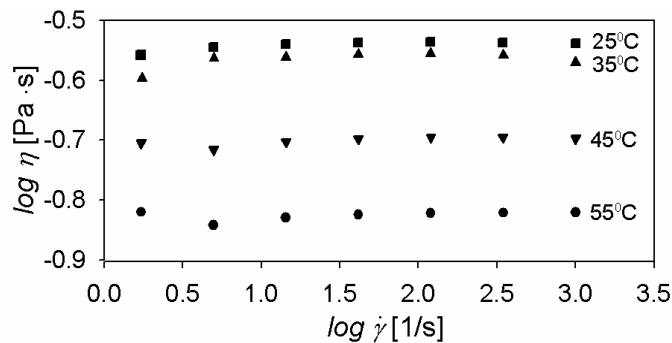

Figure 2 Logarithmic plot of dynamic viscosity as a function of shear rate for CAP of 20 wt. %, in DMAc at different temperatures.

In this context, Figure 2 plots the modification of dynamic viscosity, η, *versus* shear rate, $\dot{\gamma}$ for c= 20 wt. % at different temperatures for pure CAP. As can see, in this conditions a Newtonian behaviour appears. With increasing the concentration to 60 wt. %, the thinning effect determines the

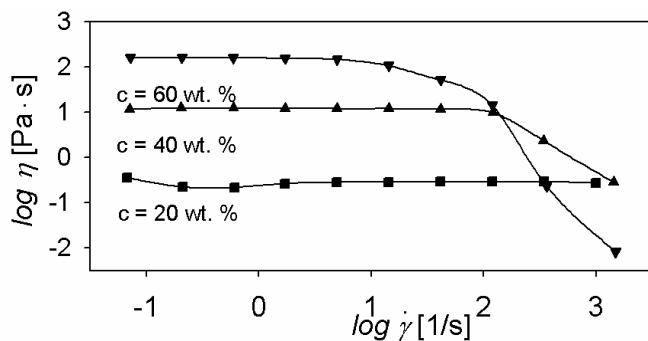dynamic viscosity reduction, under the values obtained for lower concentrations (Figure 3).

Figure 3 Logarithmic plot of dynamic viscosity as a function of shear rate for CAP of 20, 40, 60 wt. %, in DMAc at 25 $^{\circ}$C.

The interaction between the chain segments, which reflect the existence of polymer entanglements and hydrogen bonding, can be described by the activation energy, E_A, evaluated from Arrhenius equation 1 [11]:

$$\ln \eta = \ln \eta_0 + \frac{E_A}{RT} \tag{1}$$

where η_0 is zero-shear-rate viscosity, R is the universal gas constant and T is the absolute temperature. Figure 4 shows that activation energy, determines in region of shear rate with Newtonian behaviour, increases with increasing of concentration.
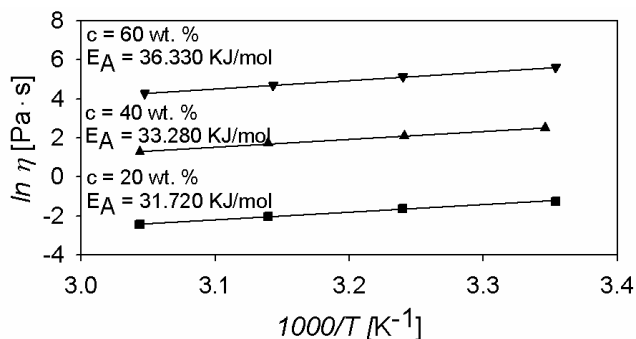

Figure 4 Plot of ln η *versus* 1000/T for CAP solutions in DMAc at different concentrations.

On the other hand, the activation energy for relaxation in polymer solutions is directly related to the positive disengagement (E_{dis}) and to the negative association (E_{ass}) contributions. In this context, the overall activation energy involving these two processes, are expressed by :

$$E_A = E_{dis} + E_{ass} \tag{2}$$

For CAP solution, according to Figure 4, the activation energy $E_A > 0$, *Edis > Eass*, and increase with increasing of

concentration. A smaller value of E_A implies a lower energy barrier for the movement of an element in the fluid. In our analysis, this barrier can be related to the interaction between the chain segments and can be determined by polymer entanglements or by specific interactions, such as hydrogen bonding.

Deviation from the Newtonian behaviour of CAP solution is analyzed also by the power law relationship expressed as follows:

$$\sigma = K \cdot \dot{\gamma}^n \tag{3}$$

where σ is shear stress, K is consistency index and n is flow index. It is known that for $n = 1$, $n < 1$ and $n > 1$ the fluid has a Newtonian, thinning and thickening behaviour, respectively. From Figure 5 it was observed that the flow consistency index decreases when increasing concentration, due to appearance of thinning phenomenon. In addition, the flow consistency index increases at lower temperatures and decreases at higher temperatures for 20-55^{0}C temperature range.
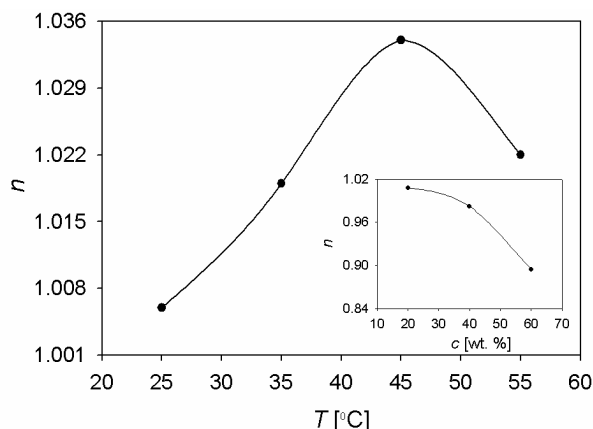

Figure 5 Flow index dependency of temperature for CAP DMAc, at c = 20 wt. % and of concentration (small plot) at 25 $^{\circ}$C.

The shear experiments performed on lyotropic HPC solutions in DMAc reveal that the viscosity-shear rate dependence for different temperatures and concentrations, respectively exhibit only Regions II and III (Figures 6 and 7, respectively). The Newtonian plateau is smaller and it is shifted to lower shear rates as concentration increases. In this context, one should mention that, below a certain critical shear rate, the isotropic solutions are Newtonian. On the other hand, viscosity versus concentration shows a maximum near the critical concentration, in the 20-60 wt. % concentration range, which designates the anisotropic phase formation. With increasing concentration the isotropic solutions show a monotonic increase in shear viscosity. Viscosity increases to a maximum when the isotropic to anisotropic transition is approached. The ordering of macromolecules in the HPC/DMAc system is associated with a viscosity lower than that of the isotropic solutions. In this context, one should mention that, below a certain critical shear rate, the isotropic solutions are Newtonian. The viscosity

peak, observed for all lyotropic polymer solutions, is a decreasing function of shear rate, ascribed to several mechanisms. For example, literature suggested a possible competition between the ordering induced by shear and that produced thermodynamically. However, other investigation found out that the correlation between the viscosity maximum and the anisotropic phase appearance is valid only when the shear rate is low, close to zero. Therefore, the viscosity at high shear rate takes lower values than the viscosity of lower concentration solutions at equivalent shear rates. Based on the viscosity *versus* concentration, the solution is in a fully liquid-crystalline mesophase for concentrations above 45.7 wt. %. Below this concentration, the solution is biphasic.
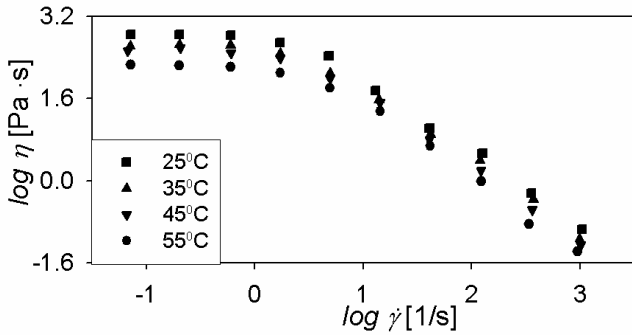

Figure 6 Logarithmic plot of dynamic viscosity as a function of shear rate for HPC of 20 wt. %, DMAc at different temperatures.
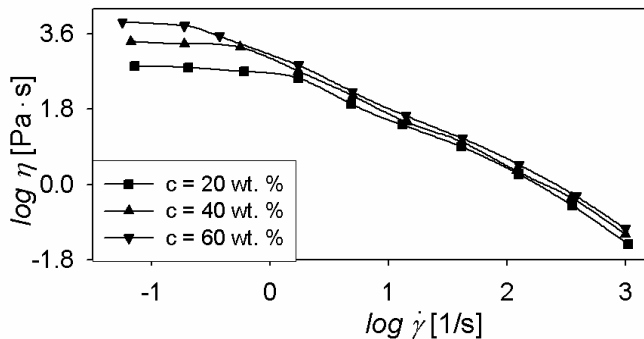

Figure 7 Logarithmic plot of dynamic viscosity as a function of shear rate for HPC of 20, 40, 60 wt. %, in DMAc at 25 ᵒC .

Figure 8 shows the plot of $\ln \eta$ versus reciprocal temperature for HPC. One can see that the solutions follow the Arhenius expression (equation 1) and that the resulting flow activation energy is influenced by the chemical structure. At the investigated concentrations, the slopes for HPC solutions are slightly increasing with concentration.
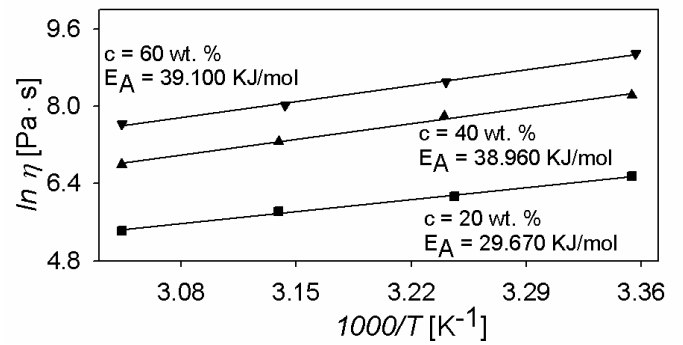

Figure 8 Plot of ln η versus 1000/T for HPC solutions in DMAc at different concentrations.

Similar remarks with those for pure samples were also established for 50CAP/50HPC blends at 40 wt. % concentration, in which Regions II and III have different expanses in function of concentration (Figures 9 and 10).
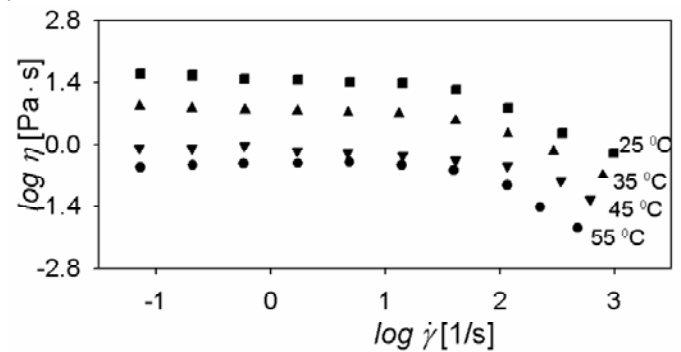

Figure 9 Logarithmic plot of dynamic viscosity as a function of shear rate for 50CAP/50HPC of 40 wt. %, in DMAc at different temperatures.
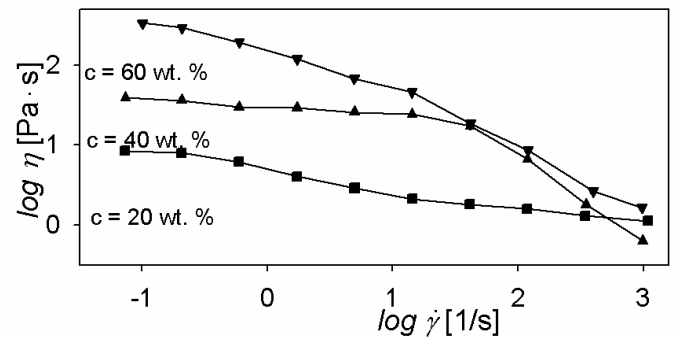

Figure 10 Logarithmic plot of dynamic viscosity as a function of shear rate for 50CAP/50HPC of 20, 40, 60 wt. %, in DMAc at 25 ᵒC.
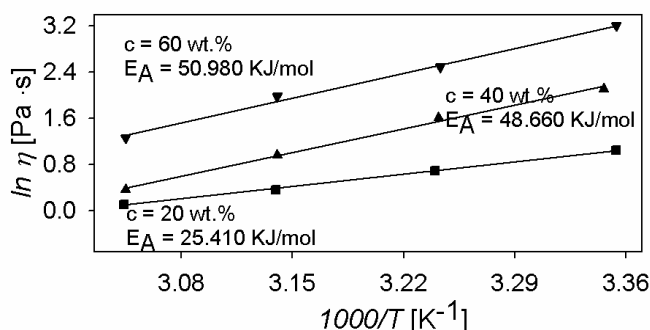
Figure 11 Plot of ln η versus 1000/T for 50CAP/50HPC blend in DMAc at different concentrations.

Figure 11 shows the plot of $\ln \eta$ versus reciprocal temperature for 50CAP/50HPC blend in DMAc. One can see that the solutions follow also the Arrhenius expression (equation 1) and that the resulting flow activation energies have positive values, corresponding to *Edis > Eass,* and depend on the solution concentrations and the chemical characteristics of components. Thus, E_A values are higher than those obtained for CAP and HPC. The reccuring anhydroglucose units reduce the flexibility of the HPC chain, resulting in highest mean activation energy values, 41.63 kJ/mol, comparatively with other two pure components.

Table 1 Storage modulus, loss modulus and frequencies for CAP, HPC and their blends of 20 wt. %; 40 wt. %; 60 wt. % concentrations at 25 °C.

CAP/HPC	G' = G''			f for G' = G''		
	c [wt. %]					
	20	40	60	20	40	60
0/100	31.6	gel	gel	2.2	gel	gel
25/75	501.2	gel	gel	4.0	gel	gel
50/50	31.6	15.9	17.8	5.6	2.0	0.4
75/25	31.6	79.4	323.6	20.0	12.6	7.9
100/0	25.1	3162.0	7943.0	15.9	39.8	44.7

Viscoelastic properties of CAP, HPC and CAP/HPC blend

The storage and loss moduli are plotted in Figures 12 and 13 as a function of frequency, *f*, for the CAP and HPC solutions, and also for the corresponding blends, at 25°C. Over the low frequency regime, the loss modulus, *G''*, is always higher than the storage modulus, *G'*, no plateau appearing in *G'* versus f curves, which is a characteristic behaviour for a viscoelastic fluid (Table 1). Generally, in this range, the storage modulus scales with frequency as $G' \propto f^2$, while the viscous modulus is linear in frequency $G'' \propto f^1$. This dependence is observed for both polymer solutions. In this context, the influence of concentration on the crossover frequency is more complex. Thus, increasing concentration from 20 wt. % to 40 wt. % leads to a decreasing in crossover frequency. At higher concentration, of 60 wt. %, Figure 13, when the liquid crystalline phase appears, the crossover frequency is higher comparatively with the case of the other two concentrations. Also, a similar dependence of the rheological moduli on frequency is observed, while the resulting slopes are smaller. Thus, for 60 wt.% concentration, *G'* and *G''* are proportional to $f^{1.347}$ and $f^{0.956}$ for CAP and to $f^{0.351}$ and $f^{0.314}$ for HPC, respectively.
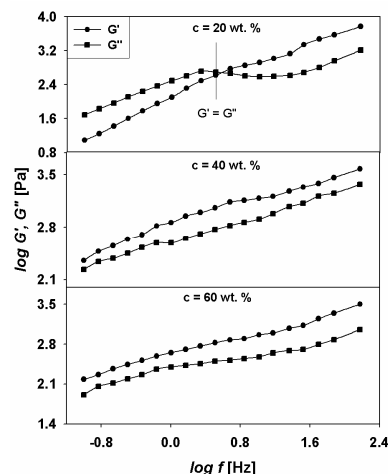

Figure 12 Log-log plots of the storage and loss moduli as a function of frequency for 25CAP/75HPC blends of 20, 40, 60 wt.%, at 25 °C.
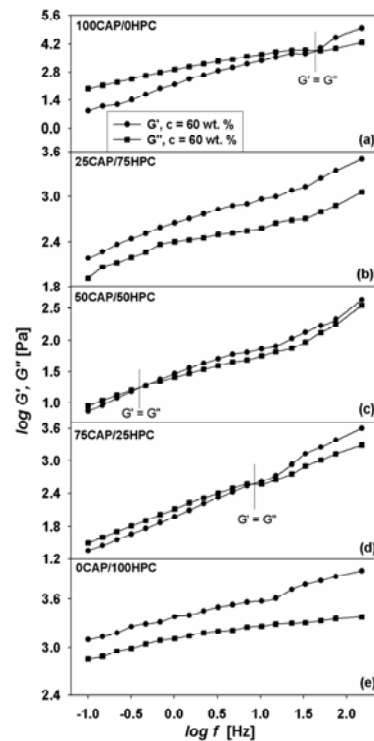

Figure 13 Log-log plots of the storage and loss moduli as a function of frequency for CAP, HPC and their blends of 60 wt. % concentrations, at 25 °C.

In case of CAP/HPC blends, the rheological moduli exhibit larger values by introducing a higher percent of HPC liquid crystal in the system. In the low frequency domain, the slopes are smaller comparatively to the pure components and decrease as the lyotropic phase becomes predominant. Also, the overlap frequency is influenced by chemical structure of components and by composition.

Investigation of the rheological properties of pure component and blends is essential for better understanding the morphology developed by CAP/HPC blends. These combined studies contribute to the knowledge on the nature of the interactions in the system, and the relation between shear deformation and texture.

CONCLUSIONS

New data on the rheological properties of cellulose acetate phthalate, hydroxypropyl cellulose solution and their corresponding blends are reported.

The casting solutions of polymers or the polymer blends show the influence of the hydroxypropyl cellulose content and concentration on the rheological properties, through dynamic viscosity and viscoelastic properties. The studies reveal by a Newtonian and thinning behaviour for CAP sample with variation of concentrations. On the other hand from variation with the frequency of storage and loss moduli for HPC pure solution and CAP/HPC blends it was observed a lyotropic liquid crystal behaviour characterized by the Regions II and III.

The activation energy determined from the dependence of viscosity on temperature shows that CAP, which possesses a higher flexibility comparatively with HPC, takes lower values, while the more rigid structures of HPC recurring anhydroglucose units, increase the activation energy. On the other hand, the presence of hydrogen bonding, which enhances rigidity in the case of CAP/HPC systems, increases the activation energy. For CAP solution, the flow consistency index is close to one value indicates a Newtonian behaviour.

The storage and loss moduli for pure component (CAP at lower concentration) exhibit the power law dependence on frequency, where the exponents are characteristic to viscoelastic fluids.

For blends with a higher concentration and content of HPC, storage modulus becomes higher than loss modulus over frequency domain, which is a characteristic of gel behaviour.

The frequency corresponding to shear moduli overlapping increases with decreasing concentration.

Knowledge on the rheological properties lies at the basis for future investigation concerning high performance of these polymeric blends.

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