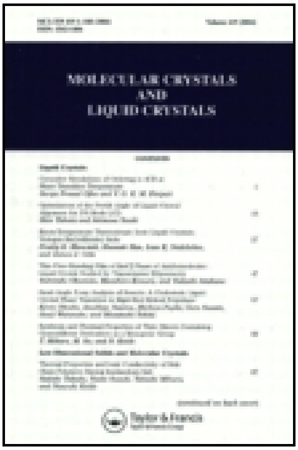

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Experimental Results on Fourier Transform Rheology of PBLG/m-cresol and HPC/Water Liquid Crystalline Solutions

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Experimental Results on Fourier Transform Rheology of PBLG/m-cresol and HPC/Water Liquid Crystalline Solutions

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In this work we present, for the first time, Fourier transform rheology data of liquid crystalline solutions of poly-γ-benzyl-l-glutamate, PBLG, in m-cresol and hydroxypropylcellulose, HPC, in water. The experimental results obtained show that, liquid crystalline polymer solutions possess an unusual behaviour in the non-linear regime, when compared with flexible polymers. For the latter, the ratio between the intensity of the third and the first harmonic, I_3/I_1 (a measurement of the nonlinear character), is an increasing function of the strain amplitude, whereas for the liquid crystalline solutions I_3/I_1 presents at least one relative maxima.

We believe that this behaviour may be linked to the existence of different flow regimes (periodic), other than the shear aligning one. Future theoretical treatment is under progress in order to clarify this phenomenon.

Keywords: First normal stress different; FT rheology; HPC; liquid crystalline solutions; PBLG

1. INTRODUCTION

The rheological behaviour of liquid crystalline polymers (LCPs) has attracted the interest of many research groups, due to its physical

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peculiarities, namely their high strength, and because of the technological importance of same materials based on them. Examples of liquid crystalline materials with outstanding properties are high modulus fibres obtained from the extrusion of lyotropic systems (like the aramid fibres, registered by DuPont, in 1971, under the trade name Kevlar®, among others [1,2]) and the high performance matrices obtained from thermotropic melts [3–6].

A large amount of work has been done in this field during the last three decades, especially in what concerns both the experimental and theoretical explanation of the dependence of shear viscosity and first normal stress difference on the shear rate, for both thermotropic and lyotropic systems [7–28]. In particular, the explanation for the appearance of negative normal stress difference has been one of the major challenges [9,10,13,15] in this field.

The importance of the behaviour under nonlinear shear is well known, for instance in processing of materials in general and of polymers in particular. It is recognized that in industrial processes non-linear behaviour is developed due to high shear deformations and high shear stresses.

The mechanical non-linear response of polymeric materials has already been studied under large amplitude oscillatory shear (LAOS) conditions, together with Fourier Transform (FT) analysis, in the seventies and eighties of the last century [29–32]. However, only in the last decade it gained a new breath due to the development of more power computational facilities.

In the nineties, an extremely sensitive data acquisition system in combination with a specific FT algorithm was applied on a commonly available rotational rheometer [33–36]. The use of this method allowed characterizing different phenomena difficult to study by classical rheometry. Detecting the crossover between linear and nonlinear mechanical behaviour in polymers solutions [34], the phase alignment kinetics in a diblock copolymer [35] and distinguishing linear from star-branched polystyrene solutions [36] are only some of the applications of Fourier transform rheology (FT-rheology). Blends of polypropylene with a liquid crystalline polymer (Rodrun LC 3000) were also studied by FT-rheology, allowing distinguishing from samples collected at different locations along the extruder, which was not possible to do with linear oscillatory rheology. These experiments also proved to be very sensitive to the LCP content (clearly more so than linear oscillatory rheology) [37,38].

In this work we present, for the first time, Fourier transform rheology data of liquid crystalline solutions of poly-γ-benzyl-l-glutamate, PBLG, in m-cresol and hydroxypropylcellulose, HPC, in water.

1.1. Theoretical Background

The mathematical concepts of FT rheology are well documented [33,35,39,40] and will not be repeated here.

Shortly, a sinusoidal strain of amplitude γ_0 is applied at a given frequency, ω_1, resulting in the formation of mechanical odd harmonics for the torque response, which are then Fourier transformed. Hence, a Fourier spectra is generated, consisting of several peaks located at the fundamental frequency ω_1 and at odd multiples of it, $3\omega_1$, $7\omega_1$, etc.

The non-linear character is obtained from the relative intensity between the third harmonic ($3\omega_1/2\pi$) and the first harmonic, and is represented by the normalized quantity $I(3\omega_1/2\pi)/I(\omega_1/2\pi) = I_3/I_1$; the higher this relative intensity the more non-linear the response.

The dependence of I_3/I_1 with the strain amplitude can be empirically described by the following equation [35]:

$$I_3/I_1(\gamma_0) = A\left(1 - \frac{1}{1 + (B\gamma_0)^C}\right) \tag{1}$$

where A, B, and C, are three adjustable parameters. Parameter A reflects the maximum intensity of I_3/I_1, C the power law dependence for small strain amplitudes and B the pre-factor (pivot point) of this power law dependency. Figure 1 presents the expected behaviour of

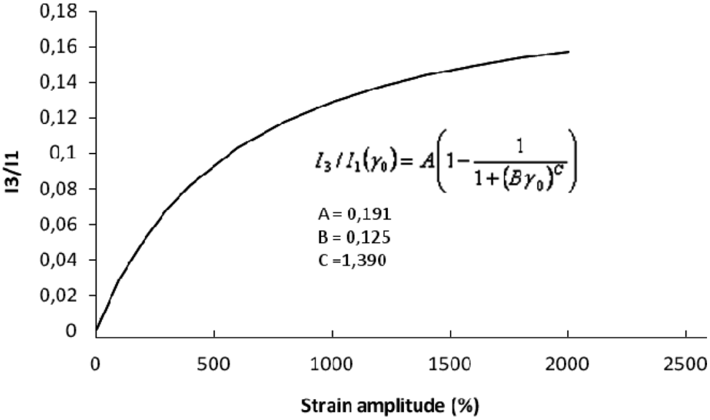


FIGURE 1 Theoretical curve of I_3/I_1 as a function of strain amplitude (the values of the parameters A, B, and C used were obtained from the fitting of equation 1, to experimental data on a 10 wt% polyisobutylene – average viscosity molecular weight of 1.1×10^3 kg/mol – solution in oligoisobutylene – molecular weight of about 190 kg/mol – at 298 K with a fundamental frequency of 0.1 Hz, [35]).

I_3/I_1 versus γ_0, taking into account equation (1), and is the usual behaviour found in flexible polymers.

2. EXPERIMENTAL

Solutions of poly-γ-benzyl-l-glutamate (PBLG, Sigma-Aldrich, viscosity molecular nominal weight of 170000 g/mol) in m-cresol (Aldrich, min 99% purity) with concentrations 6 wt% (isotropic solution) and 14 wt% (anisotropic solution). In addition, aqueous solutions of hydroxypropylcellulose (HPC, Aldrich, weight nominal molecular weight of 100000 g/mol) with concentrations 30 wt% (isotropic solution) and 50 wt% (anisotropic solution) were prepared.

The steady state shear measurements were undertaken at 24°C, using a Bohlin Gemini HR^{nano} rotational rheometer, under strain controlled mode. A cone/plate geometry with 20 mm diameter and 2° cone angle was used. Special care was taken in zeroing the normal force before the beginning of the experiment, and a pre-shear of $1s^{-1}$ during 300s was applied.

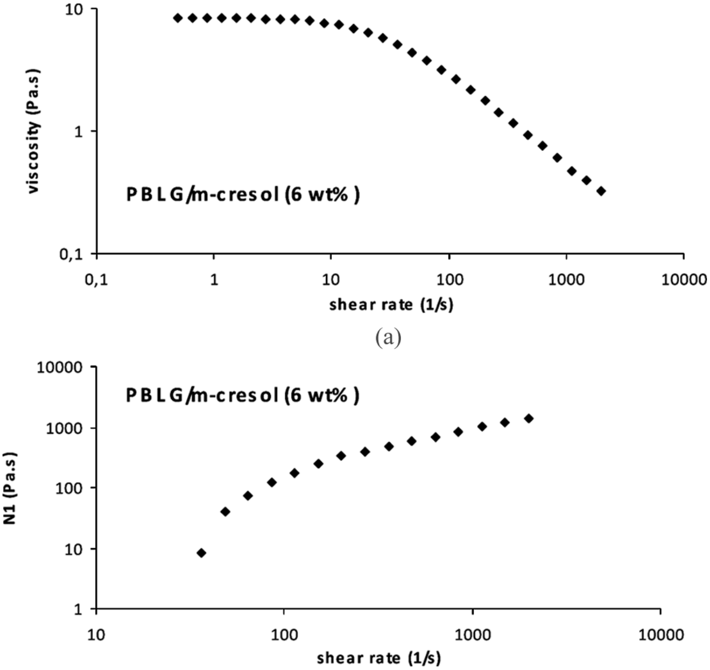
The FT-rheology measurements were carried out on a controlled strain rotational rheometer (ARES, Rheometric Instruments), using a cone and plate geometry (25 mm diameter, 0.02 rad) at 24°C. A solvent trap was used to prevent evaporation of the solvent. Time sweep measurements were carried out at a frequency of 6.28 rad/s (1 Hz), for strain amplitudes ranging from 100 to 2200%. The raw time data of the resulting torque was Fourier transformed giving rise to frequency data. In this way, the relative intensity of the third harmonic (I_3/I_1) was determined as a function of the strain amplitude. More details about this technique are available elsewhere [33–35].

3. RESULTS AND DISCUSSION

The observed steady state shear behaviour for the isotropic PBLG/m-cresol solution is shown in Figure 2. Figure 3 presents the nonlinear behaviour of the same solution as measured through the relative intensity I_3/I_1 by FT-rheology.

Figure 2 shows a common pseudoplastic behaviour for an isotropic solution, with the viscosity curve showing a first region with a quasi-Newtonian plateau, followed by a decreasing viscosity with the increase of the shear rate ($\dot{\gamma}$), and with a positive and increasing first normal stress difference (N_1) as a function of the shear rate.

Figure 3 shows the same behaviour found for flexible polymers [42,37,40,41], with the non-linear character increasing with the increase of the strain amplitude.



(a)

(b)

FIGURE 2 Viscosity, η, (a) and first normal stress difference, N_1, (b) as a function of shear rate, for a 6 wt% PBLG/m-cresol solution, at 24°C.

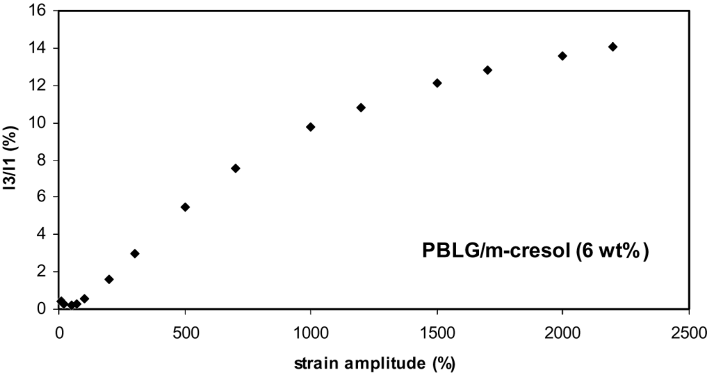
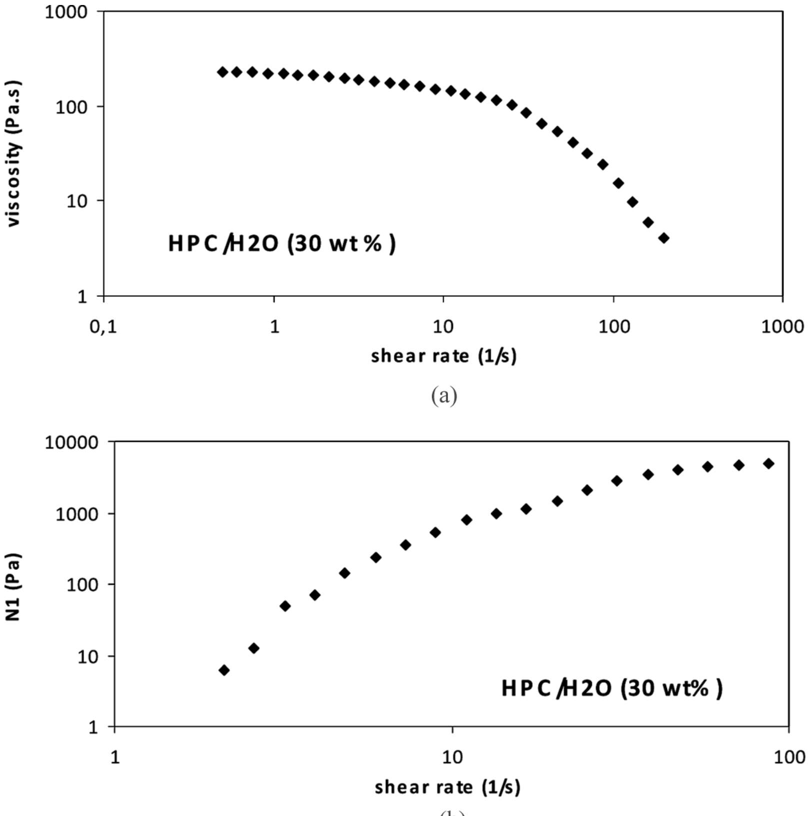


FIGURE 3 Relative intensity, I_3/I_1, as a function of the strain amplitude, for a 6 wt% PBLG/m-cresol solution, for $f = 1\,Hz$, at 24°C.

Similar results are observed for the isotropic solution of HPC/water (see Figures 4 and 5), with the exception of a decreasing I_3/I_1 with the strain amplitude, for strain amplitudes higher than about 300%. This may be explained by the alignment of the macromolecules with increasing deformation. The same decrease is expected to occur for the 6 wt% PBLG/m-cresol solution, for higher shear rates, not experimentally accessible.

The results of steady shear behaviour and FT-rheology for the anisotropic solution of PBLG/m-cresol are presented in Figures 6 and 7, and show a quite different behaviour from the isotropic solution. As expected, the flow curve is similar to the one presented



(a)

(b)

FIGURE 4 Viscosity, η, (a) and first normal stress difference, N_1, (b) as a function of shear rate, for a 30 wt% HPC/water solution, at 24°C.

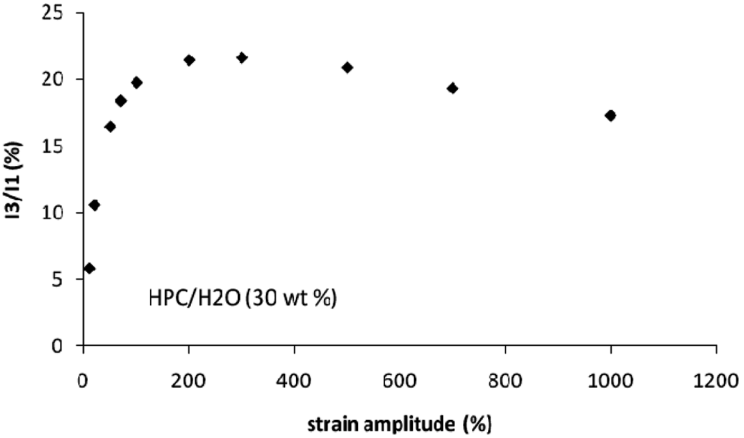
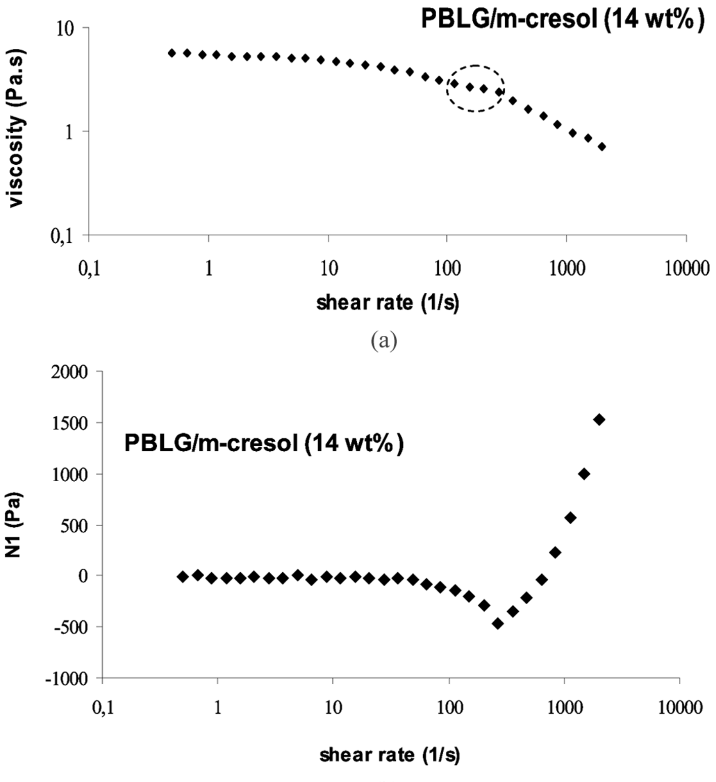


FIGURE 5 Relative intensity, I_3/I_1, as a function of the strain amplitude, for a 30 wt% HPC/water solution, for f = 1 Hz, at 24°C.

by the 6 wt% PBLG/m-cresol solution, however, it presents an *hesitation* (a small change of convexity) at a shear rate where the first normal stress difference becomes negative. This hesitation, that has been observed by several researchers [16,42], is due to a correlation between N_1 and η, and arises in the flow curve at shear rates where N_1 takes negative values, as explained by Martins [15].

N_1 as a function of the shear rate presents a behaviour typical of lyotropic solutions of liquid crystalline polymers, with a region of negative normal stress differences at an intermediate shear rate range, a small value quasi-plateau for small shear rates and positive increasing values for higher shear rates. This phenomenon is well known, namely for this same solution, with higher molecular weights (viscosity molecular weight of 238000 g/mol, for instance), for the PBLG/m-cresol [20,24] as well as for hydroxypropylcellulose (HPC)/acetic acid solutions [25] or HPC/m-cresol [27], and theoretically predicted [9,10,43,44]. In fact, according to the theories of Larson [10] and Larson and Öttinger [43], at higher 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 behaviours depending on the initial conditions. One can distinguish three types of periodic



(a)

(b)

FIGURE 6 Viscosity, η, (a) and first normal stress difference, N_1, (b) as a function of shear rate, for a 14 wt% PBLG/m-cresol solution, at 24°C.

solutions. Two of them occur when the director initially lies in the shear plane (defined by the velocity field and the gradient of the 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 intermediate shear rates), where the director suffers an oscillation 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 rates 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

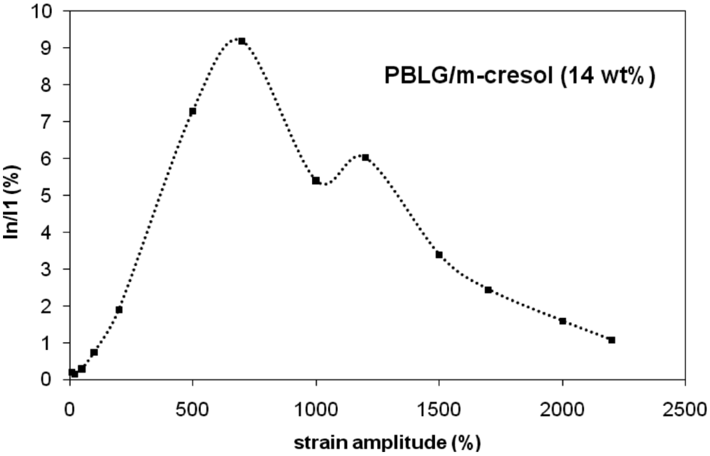


FIGURE 7 Relative intensity, I_3/I_1, as a function of the strain amplitude, for a 14 wt% PBLG/m-cresol solution, for f = 1 Hz, at 24°C (the lines are guides to the eyes).

beginning of the third region of the $\eta(\dot{\gamma})$ curve (for shear rates corresponding to the *hesitation*).

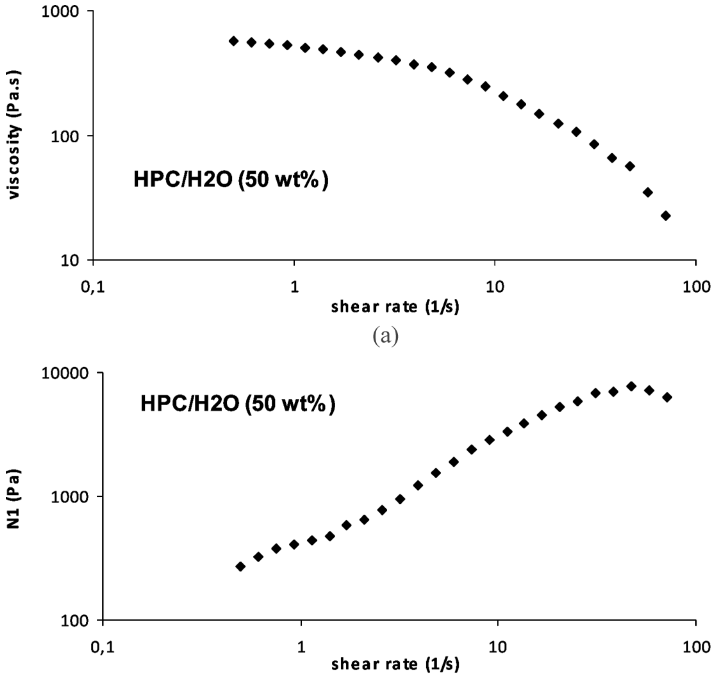
The behaviour presented in Figure 7 is also very different from the one observed for the isotropic solution, with two relative maxima, which means that, the same phenomenon that originates the appearance of negative N_1(s), may also influences the nonlinear character of the flow.

Note that the decrease observed for strain amplitudes between 700 and 1000%, is defined only with one data point, however, this phenomena is reproducible, and is also presented for the same solution analyzed at a different frequency, as well as with solutions with a different molecular weigh and/or different concentration (results not shown).

Figures 8 and 9 present the steady state shear behaviour and FT-rheology for the anisotropic solution of HPC/water, respectively.

Figure 8 shows a decreasing viscosity with the shear rate and that this solution does not present any negative N_1 region for the experimental accessible shear rate range. The absence of negative N_1 values was already reported for this solution [22].

Figure 9 shows a different behaviour from the usual one for flexible polymers, with a relative maximum at a strain amplitude of 70%. A relative maximum has already been observed in aqueous (flexible) polymers dispersions [44], however no explanation has been given for the observed maximum.



(a)

(b)

FIGURE 8 Viscosity, η, (a) and first normal stress difference, N_1, (b) as a function of shear rate, for a 50 wt% HPC/water solution, at 24°C.

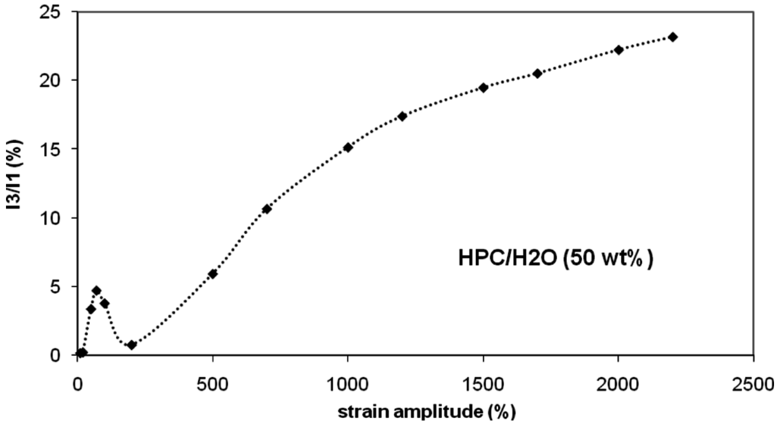


FIGURE 9 Relative intensity, I_3/I_1, as a function of the strain amplitude, for a 50 wt% HPC/water solution, for f = 1 Hz, at 24°C (the lines are guides to the eyes).

4. CONCLUSIONS

In this work we have presented the first FT-rheology study on liquid crystalline systems. The main conclusions obtained from the results presented, show that the non-linear response of PBLG/m-cresol solutions is completely different from the one presented by flexible polymers studied so far, the I_3/I_1 as a function of strain amplitude presenting two relative maxima. For the liquid crystalline solution of HPC/water a relative maximum is observed for a strain amplitude of 70%.

The same phenomena (periodic regimes) responsible for the appearance of negative first normal stress difference may also be responsible for the observed behaviour in the non-linear regime, however, a theoretical study must be performed in order to clarify this point, which will be reported in the near future.

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