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Effect of ethanol addition on the elongational flow behavior of aqueous solutions of poly(ethylene oxide)

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Summary

In this work, we explore the effect of ethanol addition on the extension thickening behavior of aqueous solutions of poly(ethylene oxide) (PEO) in porous media and opposed-jets flow. The main aspect analyzed is the formation of transient entanglements of polymer molecules, which are responsible for the sudden increase in pressure drops and apparent extensional viscosities with strain rates observed in elongational flows of PEO solutions. The results show that changing the solvent by adding ethanol modifies the solution behavior because of two effects. First, the increase in the solvent viscosity increases the disentanglement time of the transient entanglements so that the onset of extension thickening occurs at lower strain rates in the presence of ethanol. Second, ethanol solutions are poorer solvents than water for PEO. This promotes intermolecular interactions between PEO coils when the solutions are semi-dilute. The net result is a lowering of the onset strain rate for extension thickening to values that are much smaller than those expected for the same PEO chains dissolved in a higher viscosity and poorer solvent. The results also show that coil-coil interactions in solution can be detected at lower concentrations in porous media flow than in opposed jets flow.

Keywords: Poly(ethylene oxide), Ethanol, Opposed jets, Porous media, Transient networks, Semi-dilute solutions.

Introduction

The rheology of polymer solutions is significantly affected by the quality of the solvent, mainly because polymer/solvent interactions play a crucial role in the conformation of the polymer chain in solution. In addition, a change in the chemical structure and composition of the solvent might affect its viscosity and, consequently, its hydrodynamic friction with the polymer molecules. This will affect changes in chain conformation and inter-chain interactions during a specific flow event.

Solutions of high-molecular-weight polymers exhibit extension thickening in elongational flows. In particular, aqueous solutions of poly(ethylene oxide) (PEO), a flexible polymer, undergo an abrupt increase in their apparent viscosity with increases in strain rate. This has been widely documented for nearly ideal uniaxial extension induced in an opposed jets device [1], and for flow through porous media [2-4]. In flow through opposed jets, the polymer chain can experience a coil-stretch transition if the strain rate is higher than the inverse of the coil relaxation time, and if this strain rate is sustained for a long enough residence time. But the increases in the apparent viscosity are mainly due to the formation of transient entanglements of polymer molecules whose effect extends throughout a large region of the flow field and appear at even higher strain rates if the solution has a high enough concentration.

Extension thickening effects in elongational flows of flexible polymers have been observed at concentrations that are much lower than the coil overlap concentration determined by quasi-static methods (c*). The observation of intermolecular interaction effects at such low concentrations has been attributed to molecular entanglements that become active at short time scales, such as those arising in strong elongational flows [1,5]. The limiting concentration below which intermolecular effects are not observed (c^+) can be more than an order of magnitude lower than c*. As a consequence, solutions that appear to be dilute under static or shear-flow conditions might behave as semi-dilute solutions in elongational flows, yielding appreciable extension thickening.

In this work, we study the elongational flow of solutions of PEO in water/ethanol mixtures to determine how changes in the solvent quality affect the behavior of these extension-thickening solutions. Rheological experiments were performed in an opposed-jet device, and in a porous medium with PEO/ethanol solutions.

Experimental

The porous medium employed in the experiments consisted of disordered packing of monodisperse glass spheres with diameter of 1.1 mm. The porosity was experimentally determined to be 0.36. Pressure drops were recorded between the entrance and exit sections of the medium, formed by a Plexiglas cylinder of 20 mm internal diameter and 31 cm length. More details of the experimental setup and procedure are provided elsewhere [2]. The relation between pressure drop (ΔP) and flow rate is characterized in terms of the resistance coefficient, defined by

$$\Lambda = \frac{d^2 \phi^3 \Delta P}{\eta_w v (1-\phi)^2 L} \tag{1}$$

where d is the particle size, ϕ is the porosity, L is the total length of porous medium, η_w is water viscosity, and v is the superficial velocity. If the Reynolds number is defined by

$$\mathrm{Re} = \frac{\rho v d}{\eta_w (1-\phi)} \tag{2}$$

then a Newtonian fluid satisfies

$$\Lambda = A + B\,\mathrm{Re} \tag{3}$$

where A and B are constants.

The opposed jets device consisted of two capillaries (internal diameter: 0.60 mm) facing each other, separated by a distance of 1.2 mm. The capillaries were placed inside a cell with dimensions 2.5 cm x 2.5 cm x 10 cm, so that they are immersed in a relatively large volume of fluid. The solution was sucked through the capillaries by a vacuum pump. Pressure drops were recorded between a stagnant point in the cell and the exit. The set up includes an optical train to visualize birefringence patterns around the stagnation point, consisting of a 10 mW He-Ne laser, with the cell located between crossed polarizers. Details can be found in previous works [6].

The polydisperse PEO employed was provided by Polysciences (nominally $\overline{M}_w = 8\text{x}10^6$ g/gmol). Aqueous solutions of PEO were prepared by dispersing the solid polymeric powder into deionized and distilled water. In the case of ethanol/water mixtures, the polymer solutions were prepared by dispersing the polymer powder into pre-prepared ethanol/water solutions at the desired ethanol concentration. All the solutions prepared were optically transparent and no apparent signs of gel formation or phase segregation were detected. All the experiments were conducted at 22°C.

Results and Discussion

Figure 1 shows plots of resistance coefficients vs Reynolds number for PEO aqueous solutions in a porous medium for the indicated concentrations. Results for water are included for comparison purposes. The water curve exhibits a low Reynolds number plateau ($\Lambda \approx A$, Eq. 3) that corresponds to the Darcy's law regime. The polymer solutions exhibit the typical extension thickening behavior that is characteristic of highly flexible, non-free draining coils [2,3]. A pseudo-Newtonian behavior is observed at low Reynolds numbers until extension thickening sets in at a Reynolds number (Re_0) whose value decreases with polymer concentration. The extension thickening effect is due to the development of transient entanglement networks. The effect of polymer concentration is to increase the disentanglement time of the chains and therefore decrease the value of Re_0. Note that the value of the resistance coefficient at low Reynolds number increases slightly with polymer concentration. This is due to the effect of the polymer on the shear viscosity of the solutions.

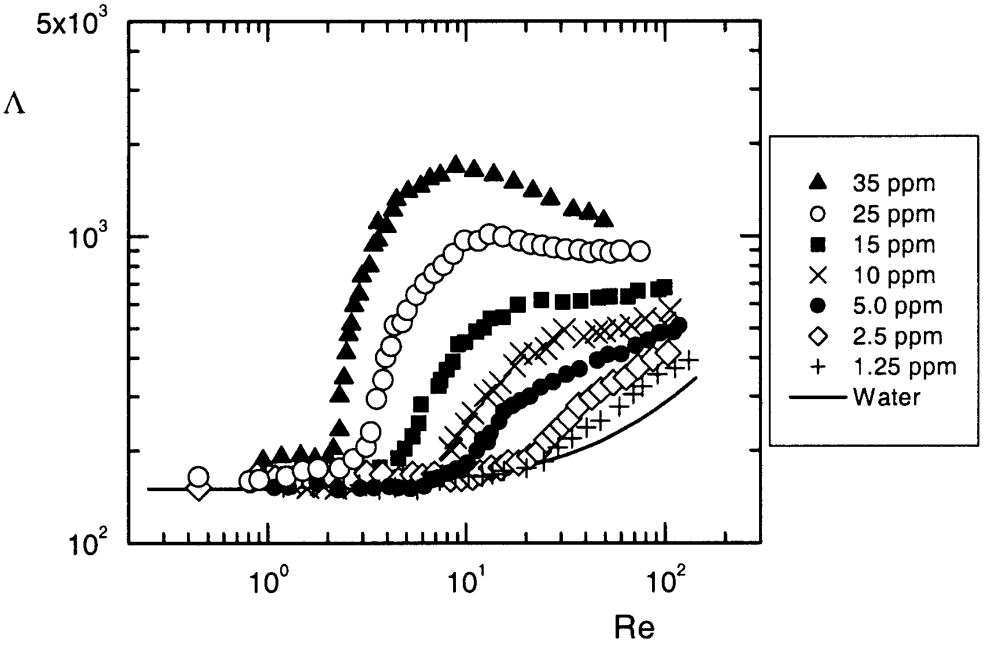


Figure 1. Resistance coefficients for water and aqueous solutions of PEO in porous media flow.

Figure 2 shows the porous media flow behavior of PEO solutions in a mixture of ethanol and water (25% v/v ethanol). The water/ethanol solution (without polymer) displays the behavior expected for a Newtonian fluid. The limiting value of resistance coefficient at low Re for this solution is about twice that of water, which is approximately the viscosity ratio between the solution and pure water. This is a consequence of the fact that, in the Darcian regime (low Re), the pressure drop is directly proportional to the viscosity. The effect of shear viscosity on the representation for resistance coefficient can be eliminated by using a modified resistance coefficient defined as

$$\Lambda^* = \Lambda \frac{\eta_w}{\eta_s} = \Lambda \frac{\Lambda_w}{\Lambda_0} \qquad \textbf{(4)}$$

where η_s is the solution's shear viscosity (for polymer solutions this corresponds to a zero-shear rate viscosity), Λ_w is the low Re resistance coefficient for water, and Λ_0 is the low Re resistance coefficient for the solution.

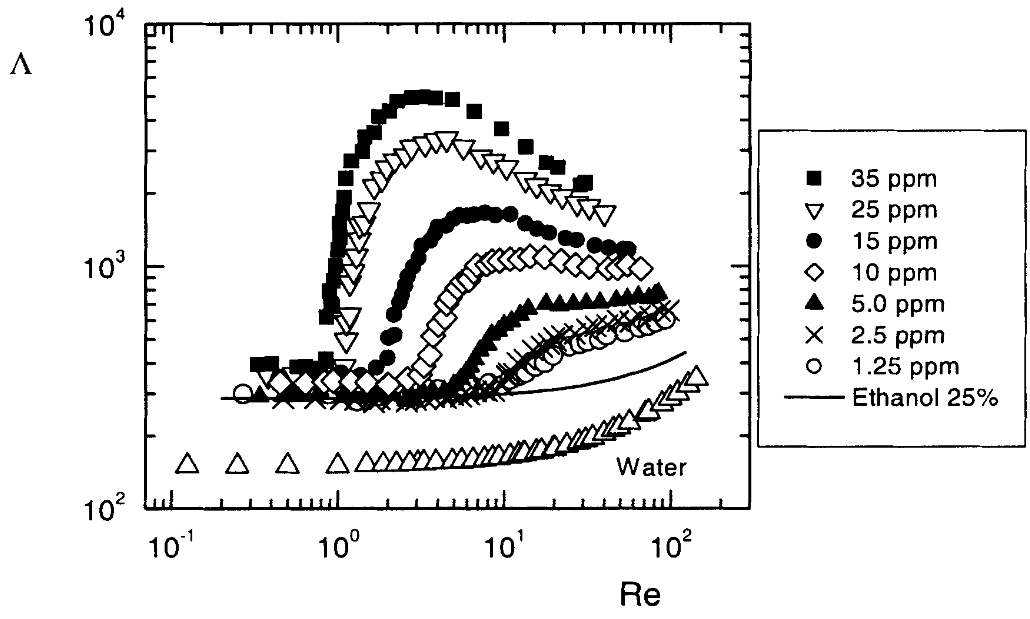
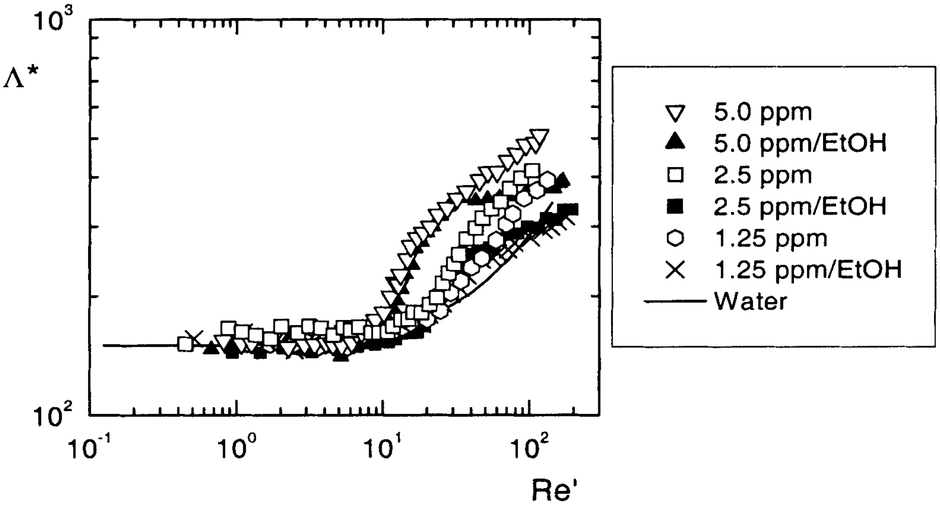


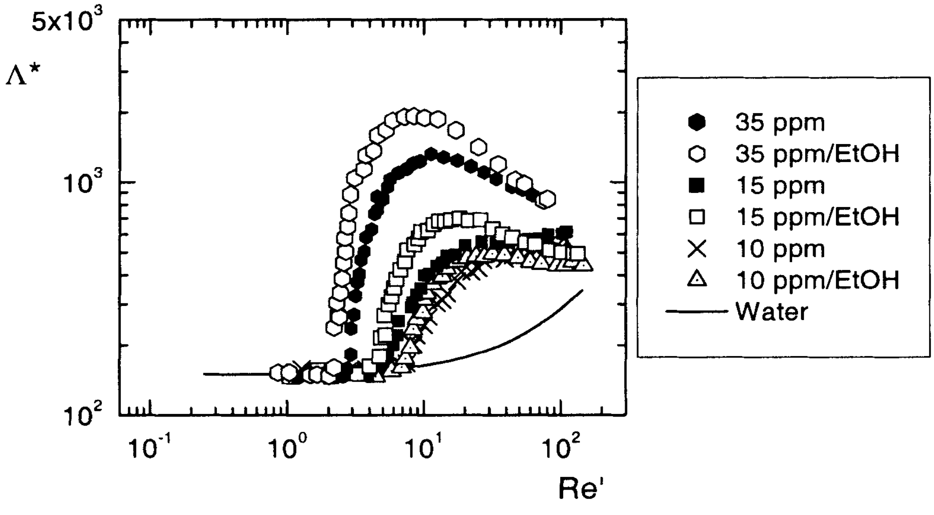
Figure 2. Resistance coefficients for PEO/ethanol aqueous solutions at a fixed ethanol concentration (25 % v/v).

A comparison of Figures 1 and 2 also shows that the onset of extension thickening occurs at lower Reynolds numbers for the solutions with ethanol when curves with the same PEO concentration are compared. If the effect of adding ethanol were only to change the shear viscosity of the solution (and not the solvent quality), one would expect Re_0 to be inversely proportional to the solution viscosity, since the relaxation time of the coil is directly proportional to the viscosity of the solution. We can then modify the Reynolds number to eliminate the effect of viscosity on the onset for extension thickening as follows,

$$Re' = Re\frac{\eta_s}{\eta_w} = Re\frac{\Lambda_0}{\Lambda_w} \tag{5}$$



(a) low concentrations



(b) high concentrations

Figure 3. Resistance coefficients for solutions of PEO in 25 % of ethanol. Note that the Reynolds number has been corrected according to Eq. (5).

In Figure 3, the data of Figures 1 and 2 have been plotted in terms of Λ^* and Re'. If the effect of adding ethanol were to change the viscosity of the solution only, we would expect Re'_0 (onset of extension thickening) to be the same for solutions with and without ethanol. However, it is well known [7] that an ethanol/water mixture is a poorer solvent for PEO than pure water. When dilute PEO solutions are considered, addition of a poorer solvent should cause a coil contraction, thus preventing interactions between coils, which should reduce the solution intrinsic viscosity and its zero-shear viscosity. However, at low PEO concentrations (Figure 3a), the onset of extension thickening seems to occur at the same value of Re' for solutions with and without ethanol. Note that the curves for water and 25% ethanol solutions of the same PEO concentration superimpose perfectly until relatively high values of Re' . This could indicate that the degree of coil contraction is not detectable in the experiments, or at least it is not significant in the elongational flow behavior.

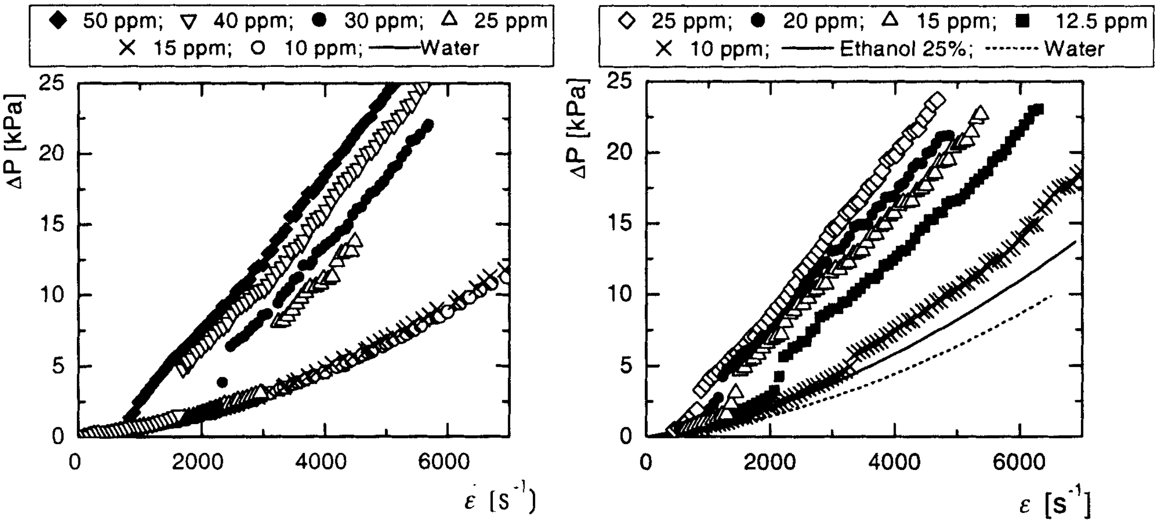
On the other hand, at higher PEO concentrations (Figure 3b), there is a noticeable shift of the onset of extension thickening to lower Re' in the presence of ethanol. In fact, resistance coefficients for ethanol solutions are consistently higher than those observed for PEO solutions in pure water. This shift, which is well beyond the effect of the solution viscosity, can only be explained in terms of the poorer solvent characteristics of the ethanol solutions. At first sight, one might expect that coil contraction induced by the poorer solvency conditions diminishes the ability of the PEO molecules to form transient entanglements, which would imply a larger onset Re' . However, in semi-dilute solutions, the fact that the polymer is dissolved in a poorer solvent should favor coil-coil interactions. This should increase the disentanglement time of transient entanglements, which allows them to be formed at lower strain rates (or lower Re'), as observed in Figure 3b. A similar effect has been reported in shear viscosity measurements of PEO solutions in water and water/ethanol mixtures by Briscoe et al. [7] They observed higher zero-shear rate viscosities for semi-dilute PEO solutions in water/ethanol mixtures than for solutions of the same PEO concentrations in pure water. The results in Figure 3b are consistent with this observation. Notice that the maximum value of resistance coefficient increases appreciably in the presence of ethanol (Figure 3b). This is the result of an increase in the entanglement density of the molecular networks as a consequence of the change in solvent quality.

To study the effect of ethanol addition to PEO/water solutions under idealized elongational flow conditions, opposed-jets experiments were performed using the same PEO as above. Figure 4a presents the pressure drop across the jets as a function of strain rate for aqueous PEO solutions. Below 25 ppm, PEO solutions exhibit a flow behavior similar to that of water. When a PEO concentration of 25 ppm or higher is employed, a sudden extension thickening behavior can be detected beyond a critical strain rate denoted $\dot{\varepsilon}_n$. For instance, in the case of 25 ppm, $\dot{\varepsilon}_n \approx 3000$ s^{-1}. Beyond this strain rate a transient entanglement network is formed that induces changes in the flow-field and chain orientation that can be monitored by observing the birefringence of the solution through crossed polars [5,6].

When PEO is dissolved in water/ethanol mixtures a change in the opposed jets rheology is observed. Figure 4b shows that extension thickening is present at PEO concentrations as low as 10 ppm. Once again the change in solvent quality is promoting coil-coil interactions that increase the disentanglement time of the networks that are formed during flow. Note that solutions that behave as dilute in pure water (10 and 15 ppm, Figure 4a) are capable of forming entanglement networks when the solvent is a 25% ethanol solution (Figure 4b).

The results in Figure 4 can be used to determine the PEO concentration below which transient entanglements cannot occur in opposed-jets flow. To do this, we start by defining a disentanglement time characteristic of the onset of extension thickening by

$$\lambda_n = \frac{1}{\dot{\varepsilon}_n} \qquad (6)$$



(**a**) deionized water

(**b**) ethanol 25 % v/v

Figure 4. Opposed jets pressure drops as a function of strain rate for PEO solutions. Values in legend represent PEO concentrations.

As the PEO concentration decreases, λ_n should decrease until it reaches zero at c^+, since this would imply that transient networks can only be formed at an infinite strain rate, and, consequently, could not be formed at lower concentrations. The values of $\dot{\varepsilon}_n$ are obtained as a function of PEO concentration from the experiments reported in Figure 4. The results are shown in Figure 5. For solutions of PEO in water (line 1, Figure 5), the extrapolated value is $c^+ = 16$ ppm. For solutions of PEO in 25% ethanol (line 2), the corresponding value is $c^+=5$ ppm. One of the causes for the increase of relaxation time when ethanol is added to a PEO solution is the increased solution viscosity. As it was done above for the porous media results, we can eliminate the effect of viscosity changes on the disentanglement time by calculating a corrected relaxation time from the following equation:

$$\lambda_{n,c} = \lambda_n \frac{\eta_w}{\eta_s} \qquad (7)$$

A plot of $\lambda_{n,c}$ as a function of PEO concentration for solutions in 25% ethanol is shown in Figure 5 (line 3). Note that the viscosity correction does not alter the extrapolated value of c^+. This shows how the enhancement of coil-coil interactions due to the poorer solvency of ethanol solutions as compared to water can noticeably affect the limit between dilute and semi-dilute regimes in opposed jests flow.

From the results presented in Figure 1 and 2 for porous media flow of solutions that are identical to those employed in opposed-jets flow, it is clear that extension thickening effects are present in porous media even for 1.25 ppm. This indicates that c^+ for porous media flow is noticeably lower than its corresponding value in opposed jets flow both when pure water or 25% ethanol are used as solvents. The successive expansions and contractions experienced by the chains that travel through multiple pores, together with the existence of multiple stagnation points in the porous medium causes an accumulation of strain in the polymer molecules that further reduces the concentration at which coil-coil interactions can be detected.

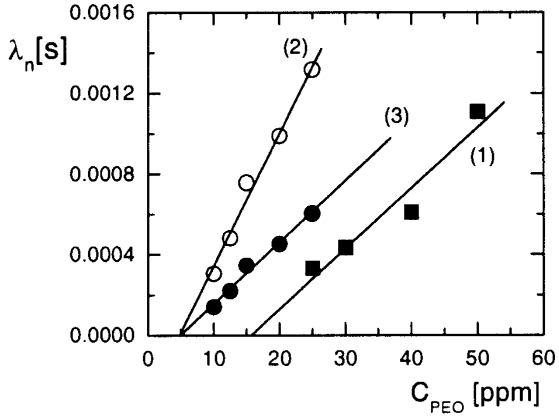


Figure 5. Disentanglement time of transient entanglements in opposed-jets flow as a function of PEO concentration, (1) PEO/water, (2) PEO in 25% v/v ethanol, (3) same as (2), but the disentanglement time has been corrected for viscosity effects, as explained in the text. Solid lines are linear fits of experimental data.

Conclusions

Changes in the solvent composition appreciably affect the elongational flow behavior of extension-thickening polymer solutions. The results obtained in this work show that, for the case of the PEO/water/ethanol system, these changes are a product of variations of the solvent viscosity, and variations in the solvent quality. Even though it is expected that ethanol solutions, being a poorer solvent for PEO than water, lead to coil contraction, the experiments performed in porous media and opposed jets flow show that the dominant effect is the enhancement of coil-coil interactions in the presence of a poorer solvent. Coil-coil interactions can be detected at lower concentrations in porous media flow than in opposed jets flow.

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