

## **Flow of solutions of hydroxypropyl guar-poly(ethylene oxide) mixtures through a porous medium**

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### **Summary**

In flow through porous media, solutions of poly(ethylene oxide) (PEO) exhibit extension thickening, whereas hydroxypropyl guar (HPG) solutions are shear-thinning at high concentrations. The results show that the extension-thickening exhibited by PEO solutions becomes less critical with increasing flow rate as the concentration of HPG in the solution is increased. At high concentrations of HPG, the presence of PEO inhibits the shear-thinning behaviour, without increasing the apparent viscosity of the solution. The presence of HPG reduces the rate and extent of degradation of PEO in the flowing solution.

**Key words:** Polymer blends, porous media, molecular flexibility, hydroxypropyl guar, poly(ethylene oxide).

### **Introduction**

The flow of polymer solutions through porous media is relevant in a wide variety of applications, such as enhanced oil recovery, gel permeation chromatography, filtration and membrane processes. To our knowledge, previous work in this field has been limited to the study of the flow of one-component solutions. The behaviour of both flexible and semi-rigid polymers has been analysed.

Flexible polymers are characterized by a sudden increase in flow resistance beyond a critical strain rate in elongational flows (extension thickening). This behaviour has been widely reported in porous media flows (1-6), in which there are important elongational components of the rate of deformation. Since the typical conformation of a flexible macromolecule in solution is the non-free-draining random coil (in  $\theta$  solvents), the flow-induced extension thickening has been explained in terms of the sudden stretching of the coils (7), and, more recently, by the formation of transient entanglements networks (4,6,8). Both theories invoke the change in draining characteristics of the coil upon unraveling to explain the increase in elongational viscosity (9).

At low concentrations, semi-rigid polymers behave as viscous Newtonian fluids. Their usual conformation in solution is an expanded coil with a high degree of draining. At high concentrations, solutions of semi-rigid polymers typically exhibit shear-thinning behaviour upon flowing through porous media, although a degree of extension thickening has been inferred from experimental data for hydroxypropyl guar (10).

Solutions of polymer-polymer mixtures have been studied in shear flows (11), extensional flows (12) and as drag-reducing agents in turbulent flows (13,14). In shear and extensional flows, the main emphasis has been to characterize the thermodynamics of the mixing process. In turbulent flows, it has been found that the

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drag reducing capability of the mixture can be appreciably better than that of the individual polymers, when at least one of the polymers has semi-rigid structure.

In this work we study the behaviour of mixtures of a flexible polymer, poly(ethylene oxide), and a semi-rigid polymer, hydroxypropyl guar, in flow through a porous medium. One of the main objectives is to assess the effect of the presence of the semi-rigid polymer on the extension thickening caused by the flexible polymer.

### Experimental

A detailed description of the experimental set up used can be found in a previous work (4). The apparatus allows the fluid to pass through a bed packed with spheres of diameter 1 mm, and average porosity of 0.4. The bed was a cylinder with an internal diameter of 1.9 cm and a packing length of 30 cm. The inlet and outlet sections were designed to ensure one dimensional flow (4).

The experiments were carried out at 20°C. Pressure drops and fluid flow rates were measured at steady state. The fluids used were distilled water, and aqueous solutions of poly(ethylene oxide) (PEO) with an average viscometric molecular weight of  $3 \times 10^6$ , and hydroxypropyl guar (HPG) with a nominal weight average molecular weight of  $2.8 \times 10^6$ .

The solutions were prepared by dispersing the polymer in water in the presence of strong stirring, in which a large vortex was formed. After complete dispersion of the solid polymer, the solution was stirred gently for approximately 24 hours. The solutions of mixtures were prepared by mixing the appropriate proportions of the one-component solutions. The hydroxypropyl guar solutions contained 10 ppm of sodium azide, used as biocide.

In dimensionless form, the pressure drop through a randomly packed, nonconsolidated porous media can be characterized by means of the resistance coefficient, defined by

$$\Lambda = \frac{\Delta P}{L} \frac{d^2 \phi^3}{\eta_s u (1-\phi)^2} \quad (1)$$

where  $\Delta P/L$  is the pressure drop per unit length of porous medium, including gravitational potential contributions,  $d$  is the particle diameter,  $\phi$  is the porosity of the medium,  $\eta_s$  is the viscosity of the solvent, and  $u$  is the superficial velocity of the fluid. For the case of one-dimensional flow of a Newtonian fluid, the resistance coefficient is only a function of the Reynolds number, defined by

$$Re = \frac{\rho_s u d}{\eta_s (1-\phi)} \quad (2)$$

where  $\rho_s$  is the fluid density. When polymer solution data are analysed, it is customary to use the viscosity and density of the solvent in the calculation of resistance coefficient and Reynolds number. For Newtonian fluids the resistance coefficient is a linear function of the Reynolds number, as expressed by the dimensionless form of the Ergun equation,

$$\Lambda = A + B Re \quad (3)$$

where  $A$  and  $B$  are empirical constants to be determined from experimental data. Values of  $A=180$  and  $B=1.8$  are commonly found for nonconsolidated media (15).

## Results and Discussion

Figure 1 shows the resistance coefficient as a function of Reynolds number for PEO solutions of various concentrations. The extension thickening is evident beyond a critical Reynolds number which we will term onset Reynolds number. Note that the results corresponding to water follow the typical trend associated with Newtonian behavior (equation 3). At 100 ppm and low Reynolds numbers the polymer solution behaves almost exactly as water. The onset Reynolds number decreases as the polymer concentration increases. This decrease is expected since the solution viscosity is increasing, which implies that the relaxation times of the PEO molecules are therefore longer (16).

The curves in figure 1 tend to reach a plateau at high Reynolds numbers. Another aspect of interest is that, for low Reynolds numbers, the results corresponding to high polymer concentrations (500 and 1000 ppm) do not reach the water value of  $\Lambda$ , but a higher value. This is due to the increase in the viscosity of the solution. Notice that the resistance coefficient is directly proportional to the pressure drop through the porous medium, and, therefore, in the viscous flow regime, it should be proportional to the solution viscosity. The behaviour exhibited by the PEO is typical of high molecular weight flexible polymers in solution (3-5).

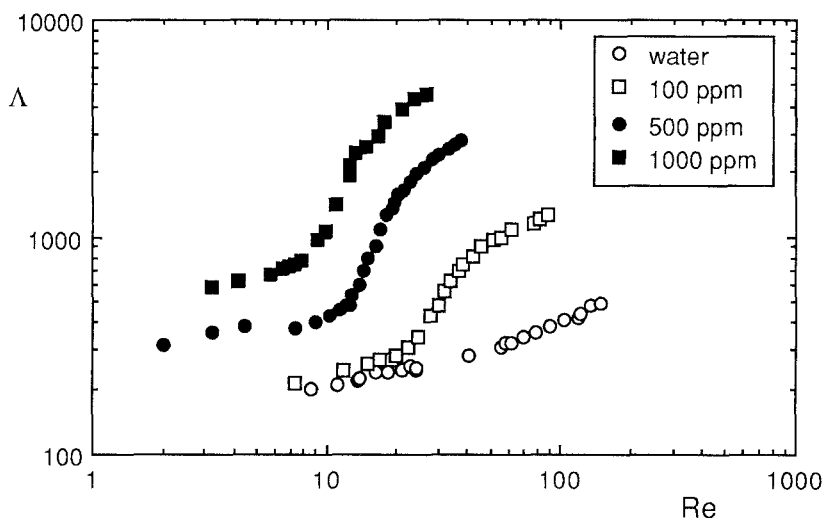


Figure 1. Resistance coefficients for PEO solutions.

Figure 2 shows the resistance coefficients of HPG solutions. These results do not exhibit the extension-thickening behavior that was present in the PEO solutions. At low to moderate HPG concentrations, the solution behaves as a Newtonian fluid with increased shear viscosity (which results in higher  $\Lambda$  values), since the usual molecular conformation in solution is an already expanded coil. At high concentrations ( $\geq 1500$  ppm) there is a definite shear-thinning effect. A comparison of these results with shear viscometry data has shown that the solution has a lower degree of shear thinning in the porous medium than in shear flows (10,17). This behaviour is typical of semi-rigid polymers (10,18).

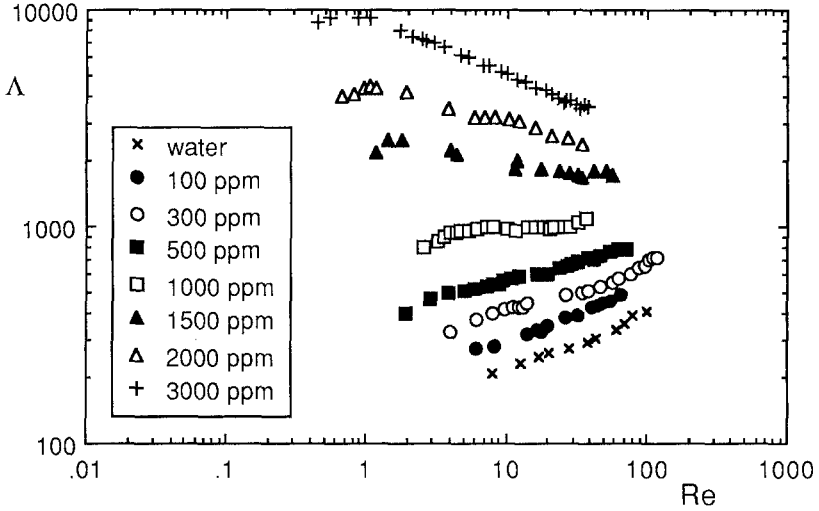


Figure 2. Resistance coefficients for HPG solutions.

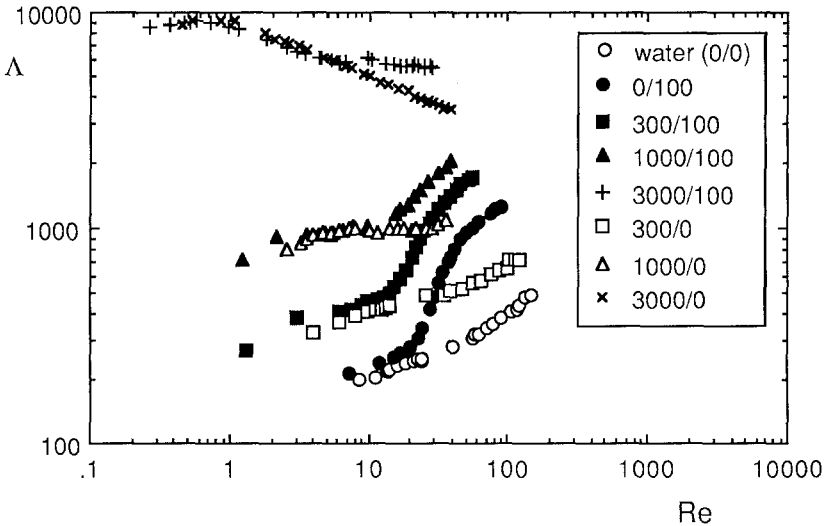
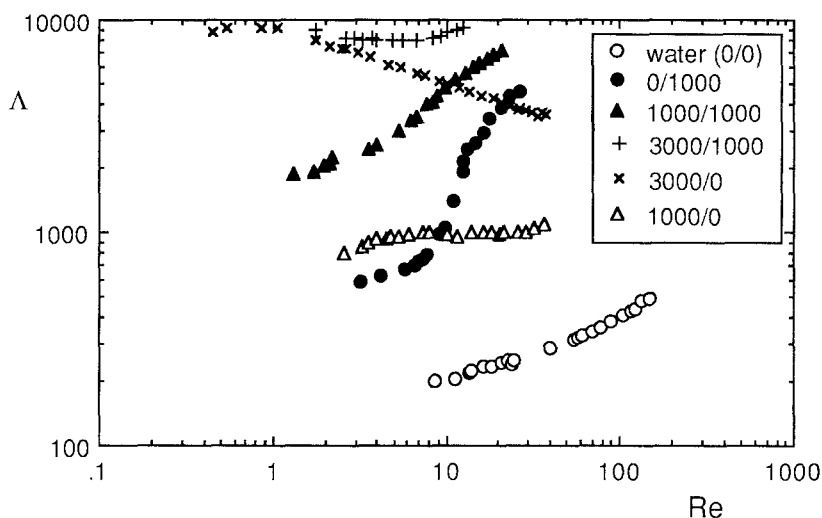


Figure 3. Resistance coefficients for solutions of HPG/PEO mixtures for low PEO concentrations. Legend shows HPG/PEO concentrations in ppm.

Figures 3 and 4 show the resistance coefficients obtained in the present work for solutions of mixtures of PEO and HPG. In figure 3 we present the results corresponding to a constant PEO concentration of 100 ppm. The resistance coefficients of the mixtures at low to moderate HPG concentrations exhibit the

extension thickening induced by the PEO. However, this effect becomes less critical with respect to Reynolds number as the HPG concentration is increased. At 3000 ppm HPG, the PEO merely inhibits to some extent the shear thinning behaviour of the HPG solution. Notice that the resistance coefficients of the blends are equal to those of the HPG solution of the same concentration at low Reynolds numbers. This is consistent with the fact that the PEO does not contribute to the shear viscosity of the blend solutions.

The results corresponding to a higher concentration of PEO (1000 ppm) are shown in figure 4. At low HPG concentrations and low Reynolds numbers, the PEO induces a noticeable change in the viscosity of the solution. As the concentration of HPG is increased in the blend, the criticality of the extension thickening decreases. Note that, at 3000 ppm HPG in the blend (3000/1000), there is a slight extension thickening at high Reynolds numbers.

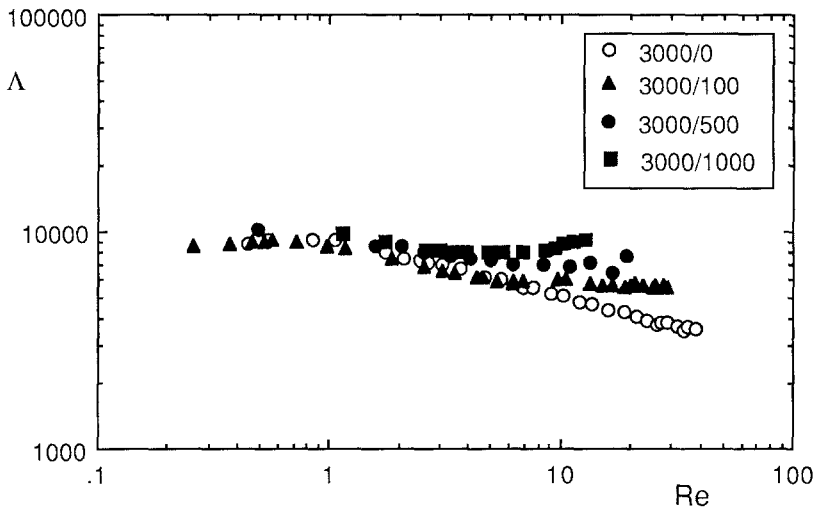


**Figure 4.** Resistance coefficients for solutions of HPG/PEO mixtures for high PEO concentrations. Legend shows HPG/PEO concentrations in ppm.

An interesting observation from the results in figure 4 is that the capability of the PEO to increase the shear viscosity of the solution at low Reynolds number diminishes as the HPG concentration is increased in the blend. In fact, for a concentration of HPG of 3000 ppm, the presence of the PEO does not alter the resistance coefficient at low Reynolds numbers. This behaviour is better appreciated in figure 5 where the results corresponding to a concentration of 3000 ppm HPG in the blends are shown. Note that, in figure 1, at the limit of low Reynolds number, the resistance coefficient for the 1000 ppm PEO solution is approximately three times larger than the water value, whereas, in the 3000/1000 blend, the same PEO concentration leads to no noticeable change in the  $\Lambda$  values at low Reynolds numbers.

The results presented above indicate that the presence of HPG in the solution has a definite effect on the extension thickening nature of the PEO. A solvent of different viscosity with respect to water would also influence the extension

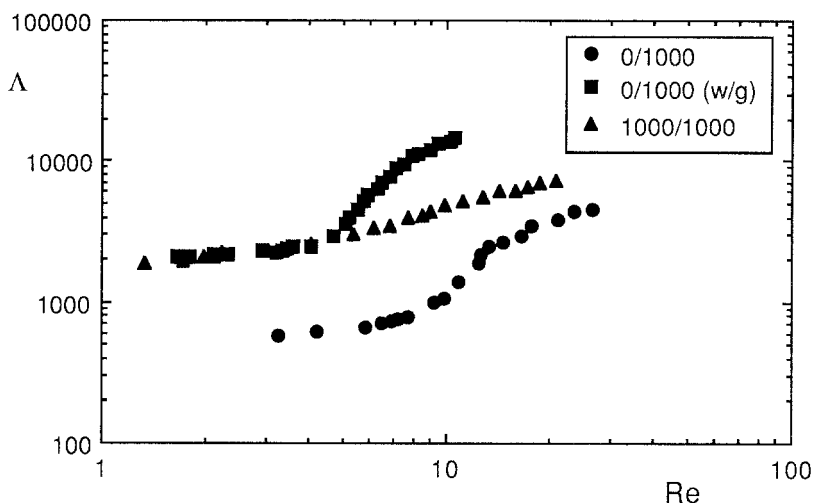
thickening of the PEO. In figure 6 we show the resistance coefficient of 1000 ppm PEO in a viscous Newtonian solvent. The solvent (60% water and 40% glycerol v/v) was chosen so that the shear viscosity of the resulting solution was equal to the viscosity of the 1000/1000 blend at low Reynolds number. Notice that the resistance coefficient at low Reynolds numbers is the same for the 1000/1000 blend and the 0/1000 (w/g) solution. In this case, the onset Reynolds number is the same for both solutions, but the rate of increase of the extension thickening is very different. This would indicate that the PEO molecules are exposed to solvents with different thermodynamic quality, if one interprets the 1000 ppm HPG solution as being the solvent for PEO in the 1000/1000 blend.



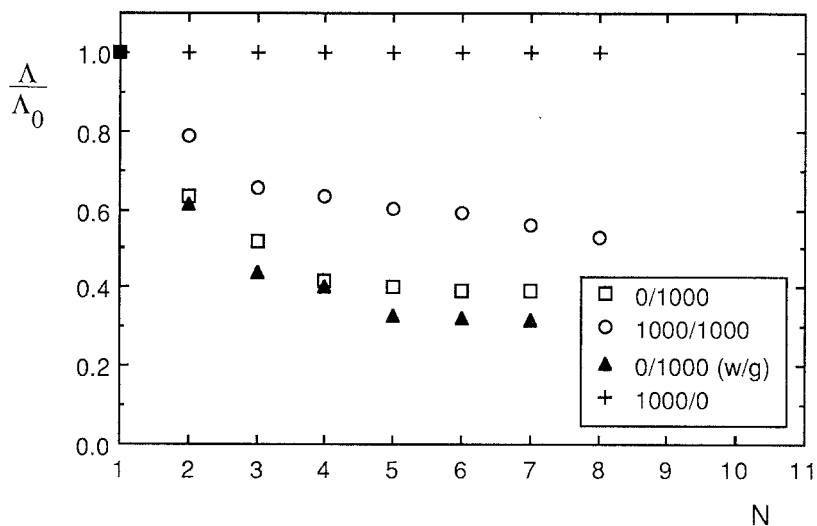
**Figure 5.** Resistance coefficients for solutions of HPG/PEO mixtures for high HPG concentrations. Legend shows HPG/PEO concentrations in ppm.

We have performed experiments to characterize the degradation of the polymers employed. The results are presented in figure 7. The experiments consisted in passing the solution repeatedly through the porous medium at constant Reynolds number. Figure 7 shows how the ratio between the resistance coefficient obtained at pass  $N$  and the resistance coefficient obtained at the first pass varies with the number of passes. The experiments were performed at  $Re=16$ , except for the PEO in water/glycerol solvent, for which the Reynolds number was 10. The HPG does not exhibit noticeable degradation, as expected from theoretical considerations based on the contour length of the molecule (17). In contrast, the PEO degrades rapidly during the first four passes. This degradation pattern is a consequence of using a Reynolds number larger than the onset value for extension thickening (5). An increase in solvent viscosity leads to an increase in the rate of degradation, since higher viscosities imply larger friction forces between the polymer molecules and the solvent (19). This behaviour can be observed in the results presented in figure 7: in the water/glycerol mixture, the degradation is faster than in pure water, even though a lower Reynolds number was used for the former. However, the 1000/1000 blend exhibits a lower rate of degradation than the PEO

solution in pure water, even though its viscosity is appreciably larger. We can gather that the presence of HPG inhibits the degradation of the PEO. This result has relevant practical interest since the use of PEO and other flexible polymers in applications such as enhanced oil recovery is sometimes severely limited by the propensity of the polymer to degrade.



**Figure 6.** Resistance coefficients for 1000 ppm PEO solutions in various environments, (w/g) refers to a solution for which the solvent is a mixture water/glycerol 60%/40% v/v.



**Figure 7.** Degradation experiments.

## Conclusions

Solutions of PEO exhibit extension thickening in porous media flow, as expected for flexible polymers, whereas HPG solutions are shear thinning at high concentrations, as expected for semi-rigid polymers. The extension thickening exhibited by the PEO becomes less critical upon the addition of HPG. Furthermore, there is a decreased capability of the PEO to increase the apparent viscosity of the solution in the presence of high concentrations of HPG. These two facts would not be expected if Newtonian solvents with different viscosities but the same solvent quality were used. The presence of HPG in the solution decreases the rate and extent of flow-induced degradation of PEO.

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