Flow of Mixtures of Poly(ethylene oxide) and Hydrolyzed Polyacrylamide Solutions Through Porous Media

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ABSTRACT: In this work, the porous media flow of polymer solutions of poly(ethylene oxide) (PEO), hydrolyzed polyacrylamide (HPAA), and their blends is investigated. Aqueous solutions of PEO exhibit critical extension thickening when flowing through porous media. HPAA solutions also exhibit critical extension thickening in excess salt environments, but their behavior changes to a more gradual extension thickening when dissolved in deionized water. The mixtures of solutions of HPAA and PEO therefore vary its porous media flow behavior, depending on the ionic environment. In deionized water, a critical extension thickening similar to that obtained with PEO is still observed when HPAA is mixed in at concentrations low enough so that its apparent viscosity does not mask the influence of PEO. In the presence of salt, only a critical extension thickening is observed, which is attributed to transient network formation of both PEO and HPAA molecules. The mixtures generally exhibit a less critical behavior and display a lower than expected sensitivity of the onset Reynolds number for extension thickening with concentration. The results presented herein indicate that interspecies molecular interactions through transient network formation and the associated flow modification play a major role in determining the complex non-Newtonian flow behavior of these polymer solutions. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 783-795, 1999

Key words: porous media flow; poly(ethylene oxide); hydrolyzed polyacrylamide; mixtures; transient networks

INTRODUCTION

The flow of polymer solutions through porous media is relevant to a wide variety of practical applications in processes such as enhanced oil recovery from underground reservoirs, gel permeation chromatography, and filtration of polymer solutions. A particularly interesting application is the use of high molecular weight polymers in enhanced oil recovery, where both flexible polymers (typically polyacrylamides in brine) and semirigid polymers (typically polysaccharides) are used.

One of the most interesting and studied aspects of the flow of polymer solutions through porous media is the increase in flow resistance obtained beyond a critical flow rate for solutions of flexible polymers. This increase has been attributed to the extensional nature of the flow field in the pores caused by the successive expansions and contractions that a fluid element experiences as it traverses the pore space, and by the presence of multiple stagnation points.^{1,2} Even though the flow field at the pore level is not an ideal exten-

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sional flow due to the relatively large lateral velocity gradients that occur close to the walls of the pores, which impose an important degree of shear and rotation, the increase in flow resistance can be referred to as an extension thickening effect. From the molecular point of view, the increase in extensional viscosity beyond a critical Reynolds number has been interpreted as a rheological manifestation of the coil-stretch transition of individual polymer molecules³ or, more recently, to the formation of transient entanglement networks.^{1,2}

The relation between pressure drop and superficial velocity in flow through porous media made up of sphere packings is commonly represented in dimensionless form in terms of the resistance coefficient, which is a dimensionless ratio between pressure drop and superficial velocity, defined by

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

In this equation, ΔP is the pressure drop over a length *L* of porous medium, ϕ is the porosity, *d* is the particle diameter, μ is the viscosity of the fluid, and *v* is the superficial velocity. If the Reynolds number is defined as

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

where ρ is the density of the fluid, then Newtonian fluids satisfy the following relation

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

Macdonald and colleagues⁴ suggested that the best fit of eq. (3) was provided by A = 180, B = 1.8, although both parameters are sensitive to the procedure used to pack the particles. A variation of $\sim 15\%$ in the values of A and B is commonly found in the literature. A result consistent with this trend is shown in Figure 1 for water flowing through a disordered packing of spheres of 1.1 mm diameter.

The nature of the non-Newtonian behavior in the flow of polymer solutions through porous media is dramatically affected by parameters such as chain conformation, polymer concentration, and molecular weight.¹ As previously described, the case of high molecular weight flexible polymers has been studied in detail in the literature.¹ The extension thickening behavior displayed by a



Figure 1 Resistance coefficients *versus* Reynolds number for water and a PEO/water solution flowing through a disordered monodisperse sphere packing.

high molecular weight ($\overline{M}_v = 3 \times 10^6$ g/mol) poly-(ethylene oxide) (PEO) in water when flowing through a disordered packing of 1.1 mm glass spheres is illustrated in Figure 1. At a concentration of 500 ppm, the solution displays a pseudo-Newtonian behavior at low Reynolds number, where its value of Λ is nearly constant. The fact that Λ was calculated using the viscosity of the solvent in eq. (1) accounts for the difference in Λ values at very low Reynolds number (which we shall term Λ_0) between the water curve and the PEO solution curve. In other words, the shear viscosity of the 500 ppm PEO/water solution is higher than that of water. If a concentration of PEO lower than 100 ppm is used, then the Λ_0 values are identical to those of water (see herein).

The rapid increase of Λ with Re beyond a specific value of the Reynolds number (usually referred to as Reynolds "onset," Re_o), as shown in Figure 1, has been recently interpreted as arising from the formation of transient entanglement networks of polymer molecules induced by the elongational flow in the pores.^{1,2} Odell and colleagues⁵ obtained experimental results in opposed-jets flow with hydrolyzed polyacrylamide (HPAA) in excess salt environment at concentrations within the typical ranges used in porous media flows. They ascertained that, after the macromolecules underwent a coil-stretch transition, the solution exhibited only small departures in flow resistance with respect to the solvent. On the other hand, beyond a critical strain rate, strong extension thickening effects were observed. These effects only occurred when transient networks of polymer molecules were formed in the flow, arising from entanglements becoming mechanically effective at time scales shorter than the network disentanglement time. The formation of transient networks was clearly observed by changes in birefringent patterns visualized between crossed polars. Odell and colleagues proposed that the degree of extension thickening observed in porous media flows was more consistent with the formation of transient entanglement networks than with the occurrence of only a coilstretch transition.

Rodríguez and colleagues² performed experiments in porous media flows with PEO solutions in a wide concentration range. They interpreted the extension thickening on the basis of the transient network hypothesis. They provide quantitative information that supports the transient network hypothesis and invalidates the coil-stretch transition theory as the only explanation of the extension thickening observed in porous media flows.¹ They showed that the strong dependence of onset strain rate on polymer concentration is consistent with that observed in opposed-jets flow when transient entanglement networks are formed. The magnitude of the change of the onset strain rate with concentration is much larger when networks are present than when the macromolecules are simply stretched in isolation in opposed-jets flow. Furthermore, a quantification of the criticality of the increase in resistance coefficient with strain rate after the onset of extension thickening shows that this effect is too abrupt to be explained by the spectrum of relaxation times of the polymer resulting from its molecular weight distribution.

Sáez and colleagues⁶ used closely monodisperse samples of polystyrene with various molecular weights, dissolved in organic solvents. The use of monodisperse polymers provides a more meaningful comparison between the results obtained in ideal elongational flow experiments and porous media flow. Sáez and colleagues compared the extension thickening obtained in porous media flows with pressure drop measurements performed in opposed jets. They found that sizable increases in resistance coefficient in porous media flow could only be observed at concentrations



Figure 2 Flow behavior of water and a PEO/water solution through an opposed-jets device.

greater than the overlap concentration required for the formation of transient entanglement networks (C^+), as detected from opposed jets rheometry.⁷ This concentration has been found to be significantly lower than the static coil overlap concentration (C^*) so that a solution perceived to be dilute from a C^* point of view could still contain weak molecular entanglements that are active only on extremely short time scales, such as those that arise in strong elongational flows.⁸ These results give strong support to the transient network hypothesis.

The onset of extension thickening for polystyrene solutions in porous media was detected by Sáez and colleagues⁶ by performing simultaneous measurements of resistance coefficients and flowinduced birefringence, averaged over several pore sizes. The increases of both parameters at the onset were practically perfect steps, a fact that lends support to the transient network theory, because the polydispersity of the polymer molecular weight (which is small but finite) and the strain rate distribution in the porous medium would lead to a measurable spread in the criticality of the effect if it were a result of isolated stretching of the macromolecules.

The analogy between flow through porous media and flow through opposed jets can be appreciated if Figure 1 (porous media results) is compared with Figure 2 (opposed-jets results), both obtained with solutions of the same polymer. In Figure 2, ΔP represents the pressure drop through the opposed-jets device, and $\dot{\varepsilon}$ is the global strain rate of the elongational flow. Data in Figure 2 were obtained by the use of an opposedjets device described elsewhere,⁹ and the sudden increase in $\Delta P/\dot{\varepsilon}$ beyond a strain rate of ~ 2.5 imes 10³ s⁻¹ was due to the formation of transient entanglement networks. Notice that $\Delta P/\dot{\varepsilon}$ is a parameter similar to Λ , because, for a given set of results, both represent the ratio between pressure drop and average velocity. The similarity between the porous media flow results and the opposedjets case is remarkable. Both sets of curves have the same overall behavior, except at low strain rates where the opposed-jets results do not achieve a plateau, a fact that is caused by inertial effects in the flow between the jets.

An interesting observation that arises from the comparison of the results in Figures 1 and 2 is the difference in the criticality of the extension thickening between opposed-jets and porous media flows. Although the extension thickening in the porous medium is more critical than what would be expected from coil-stretch transition theory,² the behavior in opposed-jets flow is even more critical. Smoothing of the resistance coefficient changes in porous media flow is a consequence of the existence of a wide range of strain rates and pore geometries.

Sudden extension thickening is not the only type of non-Newtonian behavior exhibited by polymer solutions when they flow through porous media. Another characteristic rheological phenomena in porous media flow is gradual extension thickening.¹ This behavior has been observed in HPAA solutions in deionized water,¹⁰ for polymers with molecular weights > 8 \times 10⁶. Such non-Newtonian behavior is characteristic of very high molecular weight polymers that exhibit an expanded coil conformation in solution, such as charged molecules dissolved in deionized solvents (such expanded coils will be termed semiflexible coils, because they are usually free-draining and do not exhibit the same type of molecular flexibility as ideal random coils of high molecular weight flexible molecules).

The effect of the ionic environment on porous media flow of polyelectrolyte solutions like HPAAs in water–NaCl mixtures has been widely studied in the literature.^{1,10,11} The contrasting behavior of flexible and semiflexible polymers flowing through porous media can be controlled in polyelectrolytic chains by changing the ionic environment of the solvent. Such change can be

easily conducted by adding a salt like NaCl. As the NaCl concentration is increased, thereby increasing the ionic strength of the solution, the behavior changes from that of a semiflexible polymer to the one of a flexible polymer, because the HPAA molecule tends to adopt a coiled conformation as a result of the complete screening of its anionic groups by the sodium cations.^{5,12}

Solutions of polymer blends have been studied in shear and elongational flows mainly to ascertain the effect of the flow on the miscibility of the system. For miscible mixtures, drag reduction experiments in turbulent flows through pipes^{13,14} have shown that the mixture has drag reducing capabilities that exceed that of solutions of each of the individual polymers, especially when at least one of the polymers has a semirigid structure. This motivated our previous studies of the flow of solutions of polymer blends through porous media,¹⁵ where we found that while PEO solutions exhibit extension thickening when they flow through porous media, hydroxypropyl guar (HPG) solutions were shear thinning at high concentrations. In the range of concentrations used, HPG has been found to have a semiflexible conformation.¹⁶ Results obtained with blends of PEO and HPG¹⁵ showed that the extension thickening exhibited by PEO solutions became less critical with increasing flow rate as the concentration of HPG in the blend was increased. At high concentrations of HPG, the presence of PEO merely inhibits the shear-thinning behavior, without increasing the apparent viscosity of the solution. We also found that the presence of HPG reduces the rate and extent of mechanical degradation of PEO in the flowing solution.

In this work, we study the flow of aqueous solutions of blends of PEO and HPAA. In this case, we can vary the molecular equilibrium conformation of the latter by changing the ionic strength of the solvent with the addition of NaCl. Therefore, we can prepare blends that are equivalent in extreme cases to blends of flexible-flexible polymer coils (in excess salt solutions) or flexible and semiflexible polymer coils (in deionized water solutions).

EXPERIMENTAL

The porous medium used in the experiments consisted of disordered packings of monodisperse spheres of 1.10 mm in diameter. The experimentally determined porosity was 0.368. Pressure drops were recorded between the entrance and exit sections of the medium, which has a total length of 30 cm. The experiments were conducted at 22°C. More details about the experimental set up and measuring techniques have been given elsewhere.²

The HPAA used was a high molecular weight HPAA (ALCOFLOOD 1175A, supplied by Allied Colloids, Inc., Suffolk, VA) with $M_w = 18 \times 10^6$ and a degree of hydrolysis between 35 and 40%. The ionic environment of the aqueous solutions was varied by adding NaCl. We have determined that solutions with salt yield different results, depending on the point at which the salt is added. To ensure reproducibility of the results, all solutions with salt were prepared by dissolving the polymer in powder form in a 0.5M NaCl solution. The PEO used was supplied by Polysciences, Inc. (Warrington, PA), and its average viscometric molecular weight was determined by capillary viscometry: $\overline{M}_v = 3 \times 10^6$.

All polymer solutions were prepared by carefully dissolving in deionized and distilled water (or the corresponding NaCl solution) the required quantity of polymer in powder form with minimum agitation (to avoid mechanical degradation) for 24 h. This time was needed to ensure complete dissolution of the polymer. For the preparation of the blends, the solution of each polymer was prepared using the procedure mentioned previously, and then they were mixed (after the 24-h dissolution period) and left to stand for 1 h before starting the flow experiments. All the solutions prepared were optically transparent, and no apparent signs of gel formation or phase segregation were detected. Therefore, we consider that all the HPAA/PEO/water mixtures were a single phase after preparation. Furthermore, during the flow of the polymer solutions through the porous media, since the packed bed was made up of a Plexiglas cylinder filled with glass spheres, we examined the flowing solution optically, and it always looked transparent at all points in the flow system, including within the porous medium.

RESULTS AND DISCUSSION

Porous Media Flow Behavior of PEO and HPAA Solutions

Figure 3 presents the behavior of the aqueous PEO solutions used in this work as they flow through porous media. As previously explained,



Figure 3 Resistance coefficients for aqueous solutions of PEO.

this behavior is typical of high-molecular weight flexible polymers, and has been reported previously in a wider concentration range by our group.^{1,2} Note that increases in resistance coefficient of an order of magnitude and more are present in the range of concentrations studied herein and presented in Figure 3. At the largest concentrations (500 and 1000 ppm), the curves corresponding to the solutions do not coincide with the water curves at low Reynolds number. However, the resistance coefficient approaches a constant value as Re decreases, indicating a Newtonian behavior. The higher values of Λ at low Re for high concentrations reflect an increase in the shear viscosity of the solution, as previously described.

It should be noted that, in the data presented in Figure 3, the onset Re at which the extension thickening suddenly appears (Re_{o}) decreases as concentration increases. Previous studies have indicated that such an effect cannot be accounted for exclusively by the increase in shear viscosity with solution concentration.^{6,17} We have previously shown^{1,17} that the onset Reynolds number scales with solution concentration as follows,

$$\operatorname{Re}_{o} = JC^{-c} \tag{4}$$

where J is a constant, and c has a value close to 0.5. This trend is consistent with data presented



Figure 4 Resistance coefficients for solutions of HPAA in deionized water.

in Figure 3. This is an interesting observation, because it reflects a behavior similar to that reported by Elata and colleagues¹⁸ and Naudascher and Killen¹⁹ for PEO, and also because this trend seems to be independent of molecular weight.

As previously argued, because HPAA has a polyelectrolytic nature, its flow behavior should be highly dependent on the ionic environment. Figure 4 shows Λ versus Re curves for HPAA solutions in deionized water. It can be seen that the value of the resistance coefficient is higher than that of water, even for concentrations as low as 5 ppm and from the lowest achievable Reynolds number. A gradual extension thickening behavior is observed in Figure 4 as the Reynolds number is increased. The values of Λ also increase as a function of polymer concentration, as expected. Such behavior, as already described in the Introduction, is characteristic of very high molecular weight polymers that exhibit an expanded coil conformation in solution.¹ The expansion of the coil is caused by intramolecular ionic repulsion within the chains in the absence of suitable cations to screen the negative charges, because the solvent is highly deionized. In the present case, even at 5 ppm, the solution behaves as a semidilute solution, forming transient entanglement networks at the lowest observable strain rate, because the expanded coil conformation provides connectivity of the chains at extremely low concentrations. A similar behavior has been observed in previous works in which the flow of similar solutions in ideal extensional flow fields has been reported (i.e., flow through opposed jets).⁵ In that case, birefringence measures demonstrate that the behavior is characteristic of the formation of transient entanglement networks.^{5,7}

In the presence of NaCl, HPAA tends to change from the expanded coil conformation that it adopts in deionized water to a coiled conformation, due to the screening of charges along the chain (COO⁻ groups) by the sodium cations, as previously discussed. This change occurs progressively as the concentration of salt increases, but it reaches a point at which it becomes insensitive to the addition of more salt, which corresponds to a saturation of the screening process. In this work, we will present results obtained with a salt concentration that exceeds the saturation value (0.5M NaCl) to ensure that the equilibrium conformation of the HPAA is at its most coiled state. The behavior of HPAA in excess NaCl solution exhibits the typical features of high molecular weight flexible polymers, like PEO in water. Such behavior can



Figure 5 Resistance coefficients for solutions of HPAA in water containing 0.5*M* NaCl.



Figure 6 Resistance coefficients for solutions of HPAA/PEO mixtures in deionized water for 10 ppm HPAA. Legend shows HPAA/PEO concentrations in ppm.

be seen in Figure 5 for three different HPAA concentrations in 0.5*M* NaCl solutions.

If we take into account the behavior of the polymer solutions to be mixed, we can envisage that their blends at both extreme ionic strengths will be equivalent to solutions of blends of flexible-flexible polymer coils (in excess salt solutions) or flexible and semiflexible polymer coils (in deionized water solutions). The possible interactions between the polymer coils are expected to affect the flow behavior of the solutions through the porous medium.

Flow of Solutions of HPAA/PEO Mixtures

HPAA/PEO Blends in Deionized Water

Figures 6 to 9 correspond to results obtained with solutions of HPAA/PEO mixtures in deionized water, a solvent in which the HPAA behaves as an expanded coil and PEO as a flexible nonfree draining coil.

Figure 6 shows the effect of increasing the amount of PEO added to a 10 ppm HPAA solution. There are three interesting aspects of these results that will be discussed in detail. First, upon

increasing the PEO concentration, the Λ vs. Re curve becomes more critical (i.e., the increase in resistance coefficient is more abrupt). Second, the values of Λ_0 increase as the PEO concentration increases. Finally, the Re_o is shifted to lower values upon increasing the PEO concentration. These observations are examined in more detail below.

The increase in the criticality of the extension thickening behavior as the PEO concentration increases in the presence of HPAA (Figure 6) follows the same trend as the results obtained in pure water (Figure 3). However, the critical nature of the effect is always less pronounced in the blend than in the pure PEO/water case. This is more clearly seen in Figure 7, where comparative results for a PEO concentration of 1000 ppm are presented. Note how the extension thickening of the 0/1000 curve is more pronounced than that of the 10/1000 curve. These results are consistent with our previous results on HPG/PEO blends,¹⁵ where the addition of HPG turned the extension thickening of the PEO less critical.

It is interesting to note that, even though the presence of the HPAA is increasing the value of the resistance coefficient at low Reynolds number, it is not doing so in exactly the same way a more



Figure 7 Resistance coefficients for solutions of HPAA/PEO mixtures in deionized water. Legend shows HPAA/PEO concentrations in ppm.



Figure 8 Resistance coefficients for solutions of HPAA/PEO mixtures in deionized water for 100 ppm PEO. Legend shows HPAA/PEO concentrations in ppm.

viscous solvent would (i.e., the increase of Λ_0 for PEO solutions in the presence of HPAA does not resemble a simple shear viscosity increase). This is better shown in Figure 10, where the values of the resistance coefficient measured at the arbitrary low value of Re = 6 are plotted as a function of PEO concentration. For solutions containing only PEO, the results show that for concentrations of 100 ppm or less, the Λ_0 value (taken at Re = 6) is identical to that of water, since the shear viscosity of the solution is also the same. In the case of the HPAA/PEO blends with 10 ppm HPAA, it can be seen that a solution of just 10 ppm HPAA (i.e., 10/0 HPAA/PEO) is appreciably more viscous at low Reynolds number than pure water or a 100 ppm PEO solution. However, the 10/100 HPAA/PEO blend has a higher value of Λ_0 than that of the 10/0 HPAA/PEO solution, whereas the same concentration of PEO in water does not cause an increase in Λ_0 . Therefore, the PEO molecules are not perceiving the HPAA/water around them simply as a more viscous solvent, but there seem to be interactions that are causing a higher viscosification effect at low Reynolds numbers.

Another piece of evidence that indicates that the addition of HPAA is not being merely perceived by the PEO as an increase in the viscosity of the solvent that it is exposed to is the behavior of the onset Reynolds numbers for critical extension thickening. If the Re_o values for PEO in water are compared with those of the same concentration in a 10 ppm HPAA solution, they do not change much (Table I). A Newtonian solvent with the same shear viscosity of a 10 ppm HPAA solution would have decreased the Re_o by a factor proportional to the increase in shear viscosity. This is certainly not the case herein, because the effective viscosity is changing by a factor of ~ 3 upon addition of HPAA (according to Figure 10), whereas the Re_o values are hardly changing at all. This might be a consequence of the intermolecular interactions between PEO and HPAA molecules.

The effect of increasing the concentration of HPAA in a solution with a fixed PEO concentration is seen for two PEO concentrations, 100 ppm and 1000 ppm (in Figures 8 and 9). As the concentration of HPAA is increased, a common feature can be observed in both figures: the degree of extension thickening of the PEO decreases and the effect even disappears at high HPAA concen-



Figure 9 Resistance coefficients for solutions of HPAA/PEO mixtures in deionized water for 1000 ppm PEO. Legend shows HPAA/PEO concentrations in ppm.



Figure 10 Values of resistance coefficients at Re = 6 for PEO and HPAA/PEO solutions in deionized water as a function of PEO concentration.

trations. The values of Λ at low Re are also increasing as a function of HPAA concentration, whereas the values of Λ at high Re number seem to be dominated by the maximum value of extension thickening achieved by the PEO molecules in the blend. At the maximum concentration of HPAA used (100 ppm), only the HPAA seems to dominate the flow behavior in view of its extremely high viscosifying effect. In fact, the presence of PEO has no noticeable effect: if we compare the curve 100/100 in Figure 8 with the curve 100/1000 in Figure 9, we note that they are almost identical, even though the PEO concentration has greatly increased. These results are consistent with our previous study on the HPG/PEO blends.¹⁵ In the HPG/PEO case, there was a very noticeable decrease in the capability of the PEO to increase the apparent viscosity of the HPG solutions at very high HPG concentrations.

Figure 11 shows the resistance coefficients at Re = 6 as a function of HPAA concentration for all the blends prepared in this work in deionized water. These values of Λ_0 are highly dependent on the concentration of HPAA in the solution, whereas the effect of the PEO concentration taken at a constant amount of HPAA is not very

pronounced. In fact, for high concentrations of HPAA, the values of Λ_0 are almost independent of PEO concentration. If Figures 10 and 11 are considered as representations of how the apparent shear viscosity of the solution is varying as a function of polymer concentration, we can conclude that a positive deviation from the so-called log-additive mixing rule is observed.²⁰ When polymer–polymer blends in the absence of solvent (i.e., as melts) are rheologically examined, such positive deviations are usually taken as semiempirical evidences of intermolecular interactions between the blend components.

Another aspect that should be taken into consideration is the possible change in flow patterns when transient entanglement networks are forced to flow through flow fields with predominant extensional components. The formation of transient networks in opposed-jets flow is characterized by a strong degree of flow modification, leading to flow instabilities and the loss of the stagnation point.⁷ Observations of the flow field in the pores in flow through porous media reported in the literature are contradictory. James and McLaren²¹ reported that the streamlines patterns for flow through two layers of spheres placed between flat plates did not experience any changes even after extension thickening occurred. On the other hand, Chauveteau and Kohler²² report substantial flow modification in flow through sand packs with extension thickening, including vortex formation, and point out that the streamline pattern obtained differs from that observed with Newtonian fluids at Reynolds numbers high enough that inertial effects are relevant. It is interesting that Chauveteau and Kohler argue that flow modification is a consequence of the same elastic effects that give rise to extension thickening. Deiber and Schowalter²³ performed flow visualization experiments in flow through

Table I Values of Reynolds "Onset" for Extension Thickening of Pure PEO Solutions and for Solutions of HPAA/PEO Mixtures in Deionized Water, Where the Content of HPAA Was Kept Constant at 10 ppm (Figures 3 and 6)

$C_{ m PEO}~(m ppm)$	Re _o for PEO/Water	Re _o for HPAA/PEO/Water
100	15	20
500	9.5	10
1000	8.5	9



Figure 11 Values of resistance coefficients at Re = 6 for PEO/HPAA solutions in deionized water as a function of HPAA concentration. The PEO concentrations are indicated in the legend.

periodically constricted tubes with solutions of flexible polymers. At Reynolds numbers at and slightly above the onset for extension thickening effects, they do not observe a change in the streamline patterns. A point is reached at higher Reynolds numbers at which secondary flow sets in, and vortices are formed in the expanding zones of the tubes. This occurs as the resistance coefficient vs. Reynolds number curves start to exhibit significant extension thickening behavior. Even though the evidence available is still not conclusive, and more flow visualization experiments are required, one might speculate there should be a degree of flow modification in the streamline patterns in porous media flows, especially in the regions of strong elongational flow (stagnation points and sudden contractions). This would be consistent with the transient network hypothesis.

Based on the transient network hypothesis, a speculative molecular picture for the flow behavior of the mixture can be proposed. The high apparent viscosity of the HPAA solutions has been attributed to transient network formation even at the lowest possible Re values in view of its expanded coil conformation, whereas in the PEO case transient networks are only formed beyond Re_o. In a homogeneous molecular mixture, if both types of molecules can physically interact with one another, a higher value of resistance coefficient at low Re would be obtained if a transient network is still viable, as indeed suggested by the results of the HPAA/PEO mixtures at low Reynolds numbers (Figures 10 and 11). However, the fact that the PEO component can still show a critical extension thickening phenomenon upon increasing Reynolds number is indicating that the PEO molecules within the blend are still able to stretch and interact among themselves. This is consistent with the fact that, in Figure 7 or Figure 9, when the HPAA content is low, it is clear that the extension thickening saturates for the mixtures at high Reynolds numbers at values of Λ that are nearly identical to the same values of the pure PEO solution of the same PEO content.

On the other hand, if we consider that, whenever a solution of HPAA in deionized water is present in the mixture, transient networks are formed from the lowest available Reynolds number, flow modification is probably also present. In that case, as in opposed-jets flow, the flow modification tends to reduce the elongational components of the strain rate tensor by increasing the shear components. If this is the case, even though the PEO molecules are dissolved in a higher viscosity "solvent," they might need higher Reynolds number to achieve equivalent strain rates for network formation. This might explain the small change experienced by the Re_o when pure PEO solutions are compared with HPAA/PEO solutions of low HPAA content, and also the lower degree criticality of the extension thickening in the blends (Figures 6 and 9; Table I). If the HPAA concentration is too high (i.e., 100 ppm) and therefore the Λ values generated are higher than the highest Λ values attained after extension thickening by the PEO molecules, the gradual extension thickening behavior of the HPAA dominates the behavior of the mixture, completely masking any sudden extension thickening (Figures 8 and 9).

The molecular picture previously described above could be too simplistic and may not be accurate. However, from the results obtained herein, we can summarize that the intermolecular interactions between the two types of molecules in the mixture and the flow modification effects could well be the causes of the complex non-Newtonian behavior observed.



Figure 12 Resistance coefficients for solutions of HPAA/PEO mixtures in 0.5*M* NaCl for 1000 ppm PEO. Legend shows HPAA/PEO concentrations in ppm.

HPAA/PEO Blends in NaCl Solutions

Figure 12 shows the resistance coefficient as a function of Reynolds number for mixtures of HPAA and PEO in an ionic environment of 0.5M NaCl. This figure also shows the curve of PEO in a 0.5M NaCl solution. It should be noted that the presence of salt does not alter the porous media flow behavior of PEO (compare with Figure 3), as was expected because this polymer is nonionic.

In the presence of NaCl, the resistance coefficients for the HPAA/PEO mixtures are much less sensitive to HPAA concentration than without salt. This is a consequence of the fact that, at low Reynolds numbers, the HPAA adopts a coiled conformation and, therefore, there is no transient network formation at very low Reynolds numbers for the HPAA molecules in the presence of salt. In this case, only one type of behavior is seen for the blends, the typical critical extension thickening beyond Re_o displayed by flexible coils in solution. The PEO controls the extension thickening behavior of the mixtures in Figure 12, because the PEO concentration used in this case is 1000 ppm, for which the PEO leads to a higher viscosification effect at lower Re_o than any of the HPAA concentrations used in the presence of salt (compare Figures 3 and 5).

Note that the addition of HPAA, in the HPAA/ PEO mixtures with salt, decreases slightly the onset Reynolds number and makes the extension thickening somewhat more gradual. The minor effect on Re_{o} is due to the fact that the shear component of the apparent viscosity represented by the Λ_{0} values is also very small, compared with that of the 1000 ppm PEO solution. The less critical extension thickening effect may be related to the interactions between the HPAA and PEO molecules when they form the transient networks in solution (a process that might occur simultaneously).

From the standpoint of the increase in the apparent viscosity of the mixtures, the results presented herein indicate that it is more effective to add HPAA to a PEO solution in the absence of NaCl. A comparison between some solution mixtures with and without NaCl is performed in Figures 13 and 14 for a fixed PEO concentration of 1000 ppm and two different HPAA concentrations: 10 and 50 ppm. A more effective viscosification at low Reynolds number is always achieved in the blends without salt. At higher flow rates, the extension thickening of the PEO dominates regardless of the NaCl content. Therefore, in the



Figure 13 Comparison of porous media flow behavior of 10/1000 HPAA/PEO mixtures in deionized water and in 0.5*M* NaCl. Legend shows HPAA/PEO concentrations in ppm.



Figure 14 Comparison of porous media flow behavior of 50/1000 HPAA/PEO mixtures in deionized water and in 0.5*M* NaCl. Legend shows HPAA/PEO concentrations in ppm.

absence of NaCl the apparent viscosity of the solution is generally higher in all the Reynolds number range explored in our experiments than in the solutions with added salt.

CONCLUSIONS

The solutions of mixtures of HPAA and PEO vary its porous media flow behavior, depending on the ionic environment because of the polyelectrolytic nature of HPAA.

In deionized water, a critical extension thickening behavior corresponding to the PEO component is still observed when the HPAA concentration is low enough so that its apparent viscosity does not mask the effect. The extension thickening behavior is not as critical in the blend as in the pure PEO solutions. These results were rationalized in terms of the changes experienced by the transient networks formed during the flow process and their flow modification effects.

In the presence of salt, only a critical extension thickening is observed attributed to transient network formation of both PEO and HPAA, and a minor effect was observed in the resistance coefficient at low Reynolds number. Therefore, from the standpoint of the increase in the apparent viscosity of the mixtures, our results indicate that it is more effective to add HPAA to a PEO solution in the absence of NaCl.

The results presented herein on the porous media flow of solutions of HPAA/PEO blends indicate that intermolecular interactions and associated flow modification effects play a major role in determining the complex non-Newtonian flow behavior of these polymer solutions.

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