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Flow-induced degradation of hydrolyzed polyacrylamide in porous media

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Summary

In this work we present an experimental study of flow-induced degradation of hydrolyzed polyacrylamide in aqueous solutions flowing through porous media. The degradation is analyzed by passing the solution repeatedly through the medium at a constant flow velocity and the degraded solution is then characterized by porous media and opposed jets flows. When the polyacrylamide is dissolved in deionized water, it exhibits a gradual extension thickening in the flow through porous media and opposed jets. In this case, the polymer degrades as it passes through the porous medium even at relatively low flow rates. When the polyacrylamide is dissolved in an NaCl solution, it exhibits critical extension thickening in porous media flows, and it only degrades at Reynolds numbers that are higher than the onset of the extension thickening behavior. Chain degradation is therefore only encountered when extension thickening is produced. The results also show that the extent of degradation decreases as the pore size decreases.

Key words: porous media, polyacrylamide, mechanical degradation, opposed jets.

Introduction

One of the most important aspects in the application of polymer additives is their susceptibility to mechanical degradation. It has been widely recognized that semi-rigid molecules such as xanthan gum and hydroxypropyl guar are more stable to flow-induced degradation than flexible polymers such as poly(ethylene oxide) (PEO) or hydrolyzed polyacrylamide (HPAA). Flow-induced degradation might limit the applicability of a given polymer to specific applications such as enhanced oil recovery.

The hydrodynamics of porous media flows is generally expressed in terms of the resistance coefficient, which for sphere packings is defined by

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

where ΔP is the pressure drop over a length L of porous medium, ϕ is the medium porosity, d is the particle diameter, μ is the solvent viscosity and v is the superficial velocity. The Reynolds number is defined by

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

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where ρ is the density of the fluid. It has been established that Newtonian fluids follow the Ergun equation

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

where the first term dominates in the viscous flow regime ($\mathrm{Re}<1$). Note that in the viscous flow regime the resistance coefficient can be interpreted as a dimensionless apparent viscosity of the solution in the porous medium since it is proportional to the ratio between pressure drop and superficial velocity.

Solutions of flexible polymers exhibit extension thickening behavior in porous media flows (1). This behavior is characterized by a Newtonian plateau at low Reynolds numbers, a sudden increase in resistance coefficient at a certain value of the Reynolds number, which represents the onset of the extension thickening effect, and a second Newtonian plateau at higher Reynolds number. The extension thickening is a result of the formation of transient entanglement networks of polymer molecules induced by the stretching action of elongational components of the flow field at the pore level (1). As will be documented here, extension thickening effects are generally accompanied by flow-induced degradation.

Maerker (2) recognized that the degradation of viscoelastic polymer solutions as they flow through porous media is caused by elongational stresses. The degradation was characterized in terms of the screen factor loss of the solution after it was passed through the medium. The screen factor is defined as the ratio between the flow time of the polymer solution and the flow time of the solvent as a given volume of the solution passes through a pack of five 100-mesh screens. The screen factor losses measured by Maerker on HPAA/salt solutions indicated that degradation only occurred beyond a certain value of the strain rate, and that degradation increases gradually with strain rate after this onset. Maerker also found that screen factor loss increased as the ionic strength of the solution was increased upon addition of NaCl to HPAA solutions.

A different method to characterize mechanical degradation in porous media flows was employed by Farinato and Yen (3). They measured the Λ vs. Re curve of the original polymer solution. Afterwards they passed fresh solution at a constant Reynolds number through the medium and recorded the Λ vs. Re curve of the effluent. A difference between the onset Reynolds number for extension thickening (Re_o) of the two curves was interpreted as a result of mechanical degradation.

The influence of particle size on flow-induced degradation was studied by James and McLaren (4) who reported that degradation of PEO increased with increases in the particle size. They quantified degradation by comparing the values of pressure drop across different lengths of the porous bed. The pressure gradient progressively decreased along the length of the medium due to degradation. Later, Käser and Keller (5) reported in a very similar study that the observation by James and McLaren could be erroneous because their measurements did not include the extensive degradation that occurred upstream of their first measuring point. The experiments performed by Käser and Keller suggested that degradation extent increased as the particle size decreased. Chauveteau (6) reported similar results for solutions of PAA in water.

Haas and Kulicke (7) have reported data on mechanical degradation in porous media flows of solutions of HPAA and closely monodisperse atactic polystyrene (aPS). The mechanical degradation of the polymers was quantified through resistance coefficient changes and, for the aPS, it was supported by measurements in the change of the average molecular weight of the polymer after the solution was passed through the medium. They determined that appreciable molecular weight reduction only occurred when the solution was circulated at Reynolds numbers larger than those required for the onset of extension thickening.

In a previous work (8), we performed experiments to characterize the degradation of PEO in porous media flows. PEO solutions were repeatedly passed through a porous medium at the same Reynolds number and the resistance coefficient in each pass was recorded. Degradation only occurred when extension thickening effects were present. Furthermore, the resistance coefficient decreased with the number of passes until it reached an asymptotic value, which indicates that eventually all the solution was degraded to a uniform final state. When this final solution was passed through the medium, the onset Reynolds number for extension thickening was equal to the Reynolds number at which the solution was degraded. This result leads to the conclusion that all the macromolecules that participate in the extension thickening effect are eventually degraded in the flow field. A similar conclusion was obtained by Sáez et al. (9) working with closely monodisperse aPS in a mixture of organic solvents. It is interesting to point out that a similar behavior has been observed in elongational flow experiments in opposed jets when transient entanglement networks produce extension thickening (10,11).

In this work we study the flow-induced degradation of HPAA in porous media. The extent of polymer degradation is quantified in terms of reduction of resistance coefficients, and also by using an opposed jets device as a means of characterizing the apparent extensional viscosity of the polymer solutions. The effects of Reynolds number, ionic environment and particle size on degradation are analyzed.

Experimental

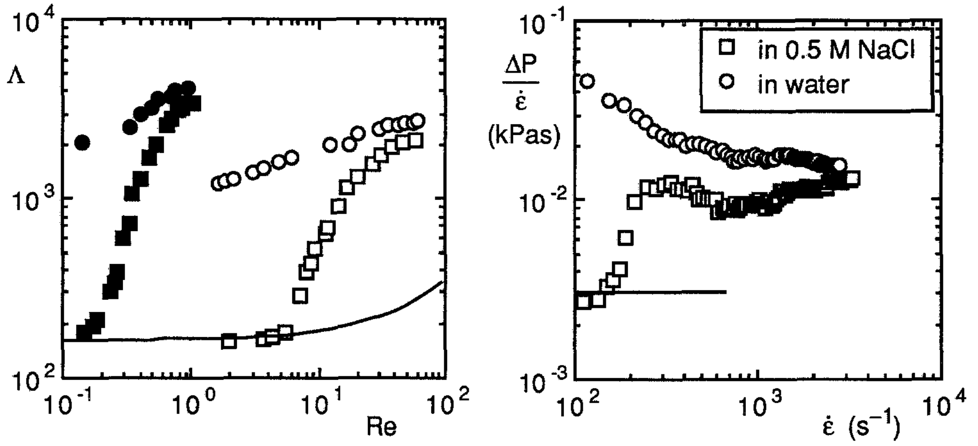
The porous media employed in the experiments consisted of disordered packings of monodisperse spheres. Two different particle sizes were used: 1.10 mm and 0.27 mm. Both packings had porosities of 0.38. Pressure drops were recorded between the entrance and exit sections of the medium, which has a total length of 30 cm. More details about the experimental set up and measuring techniques have been given elsewhere (1).

The opposed jets used had internal diameter of 0.35 mm and jet separation of 0.57 mm. The experimental set up has been described elsewhere (12). The apparatus can control and measure strain rates while monitoring the pressure drop across the jets.

The polymer employed was a high molecular weight hydrolyzed polyacrylamide (ALCOFLOOD 1175A, provided by Allied Colloids Inc.) with $\overline{M}_w=18\times10^6$ and a degree of hydrolysis between 35 and 40%. The polymer concentration was 50 ppm in all the experiments. 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. In order to assure reproducibility of the results, all solutions with salt were prepared by dissolving the polymer in powder form in a 0.5 M NaCl solution. All the experiments were performed at 22°C.

Results and Discussion

The effect of ionic environment on the flow of HPAA solutions through porous media is illustrated in figure 1a. As NaCl is added to the polymer solution, the behavior of the HPAA changes from that of a semi-flexible polymer to that of a flexible polymer, since the macromolecules adopt a coiled conformation in the presence of salt due to the screening of its anionic groups by the sodium cation. These anionic group maintain the macromolecule in a highly-expanded state in the absence of salt (13,14). We have determined that NaCl addition beyond 0.5 M does not change the resistance coefficient. This indicates that at this salt concentration ionic screening has reached a saturation. The solutions with salt exhibit the typical extension thickening effect characteristic of flexible polymers (1). In the absence of salt, the extension thickening behavior is still present but the increase in resistance coefficient with Reynolds number is gradual.

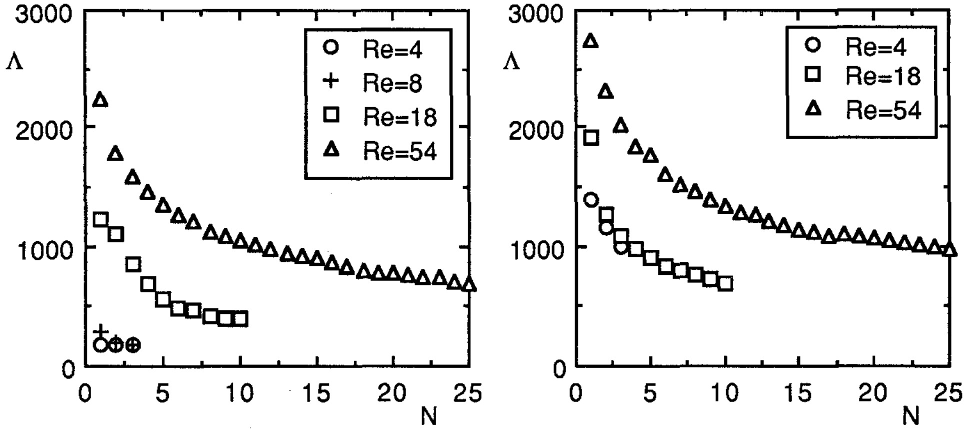


(a) (b)

Figure 1. Hydrodynamics of water and 50 ppm HPAA solutions. Solid lines are curves obtained for water. (a) Resistance coefficients in porous media flow, circles: HPAA in water, squares: HPAA in 0.5 M NaCl; filled symbols: d=0.27 mm, open symbols: d=1.10 mm. (b) Opposed jets flow.

The behavior of HPAA solutions was also studied in opposed jets flow. Pressure drops were obtained as a function of strain rate ($\dot{\varepsilon}$). The results are presented in figure 1b. The ratio of pressure drop to strain rate can be interpreted as an apparent elongational viscosity so that it is similar to what the resistance coefficient represents in porous media flows. Notice that the trends in figure 1b resemble closely those obtained in porous media flow (figure 1a) with the exception of the decreasing trend exhibited by the pressure drop to strain rate ratio of the solution without salt, which could be due to mechanical degradation in the jets. This confirms that the extension thickening behavior exhibited by the solution with salt in porous media flows is mainly due to the elongational nature of the flow field in the pores. Quantitative comparisons between opposed jets and porous media flow have not been performed since in the disordered sphere packing there is a wide distribution of local strain rates owing to the complexity of the geometry at the pore level. Furthermore, the flow in the porous medium is not as close as ideal uniaxial extension as the opposed jets flow since the elongational flow in the porous medium occurs as a result of successive contractions and expansions of the flow path, and the existence of stagnation points. There is also an important shear component of the flow in the pores.

The mechanical degradation of HPAA induced by the flow in the porous medium was studied by repeatedly passing the polymer solutions through the porous medium at a constant Reynolds number while the pressure drop was being recorded. Figure 2 shows the variation of resistance coefficient with the number of passes (N) for solutions with and without salt. The Reynolds number in the legend represents the value at which the solution was passed through the porous medium. The solutions without salt experience degradation in all the range of Reynolds number studied, figure 2b, whereas the solutions with salt only exhibit changes in the resistance coefficient when the Reynolds number exceeds the onset for extension thickening of the original solution (Re_0=6, see figure 1a), figure 2a. The decrease in the value of Λ at constant Reynolds number indicates that the polymer is being progressively degraded in the pores at an average strain rate that should be proportional to the Reynolds number. Such strain rate for fracture is expected to depend on molecular weight (15). Therefore, when most of the molecules with molecular weight greater than or equal to that for which the given strain rate is the fracture strain rate have broken, the resistance coefficient becomes constant.

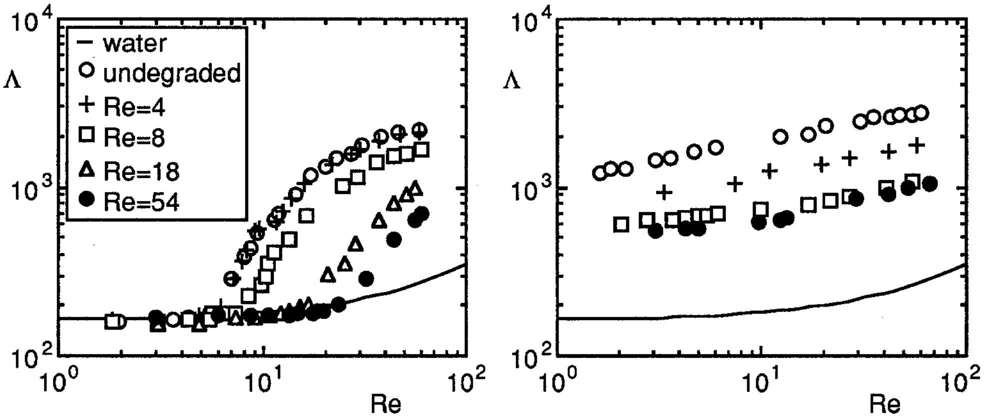


(a) Solvent: 0.5 M NaCl (b) Solvent: deionized water

Figure 2. Decrease in resistance coefficient during porous media degradation of 50 ppm HPAA solutions at constant Reynolds number (d=1.10 mm).

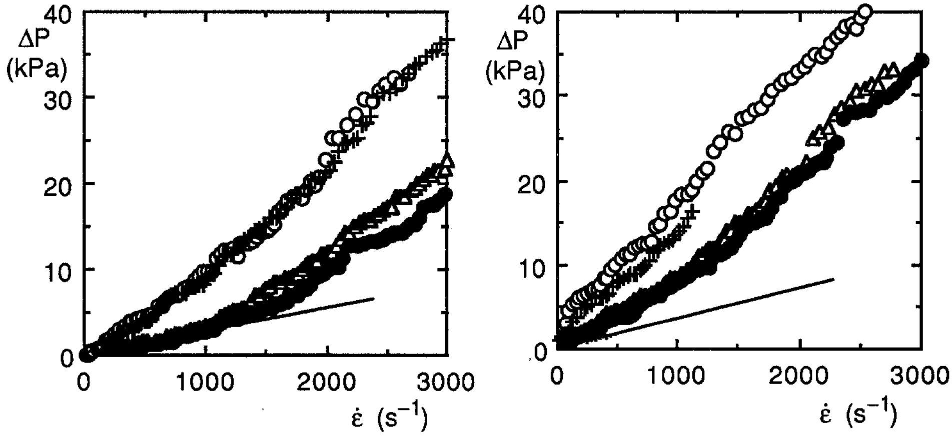
The mechanical degradation can also be assessed by the variation in the Λ vs. Re curve of the solution obtained before and after it has been repeatedly passed through the porous medium. Figure 3 shows such variations for solutions with and without salt. In the presence of salt (figure 3a) the onset of extension thickening is shifted to higher values of Reynolds number after degradation occurs. The increase of onset Reynolds number can be interpreted as an increase in the critical strain rate for the formation of transient entanglement networks of macromolecules. Any increase in the onset Reynolds number therefore indicates a decrease in the average molecular weight of the polymer. The results in figure 3 also confirm that the polymer is appreciably degraded only when the Reynolds number at which it is passed through the medium is higher than the onset of extension thickening. In fact, the value of the onset Reynolds number after degradation is close to the Reynolds number at which the solution is degraded if enough number of passes are allowed. Parallel results have been previously obtained for PEO (8), and for aPS (9). In the absence of salt (figure 3b) degradation occurs even at low Reynolds numbers. Notice that in this case the behavior of the resistance coefficient curves is not altered after degradation; the effect of the decrease in the molecular weight is to yield a lower level of viscosification.

The degraded solutions whose porous media characterization is presented in figure 3 were also passed through the opposed jets device. The results are shown in figure 4. In the presence of salt (figure 4a) the undegraded solution separates from the Newtonian behavior at very low strain rates (see also figure 1b). The solutions degraded at high Reynolds number follow the behavior of water until the critical strain rate at which transient entanglement networks are formed, which increases as the Reynolds number increases. Note that the solution passed at Re=4 is indistinguishable from the undegraded solution. In the absence of salt (figure 4b), degradation is once again evident even for the lowest Reynolds number employed. These results are consistent with the porous media results discussed above.



(a) Solvent: 0.5 M NaCl (b) Solvent: deionized water

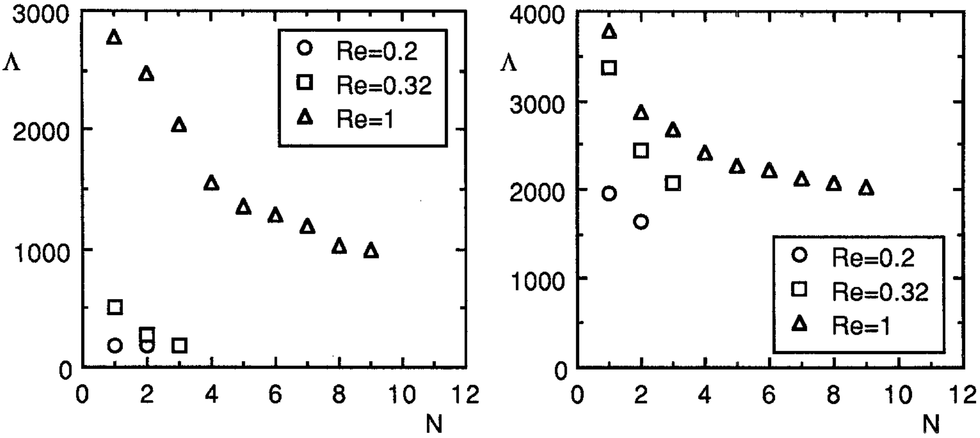
Figure 3. Resistance coefficients of original and degraded 50 ppm HPAA solutions. Number of passes for degraded solution is the maximum for which results are presented in figure 2 (d=1.10 mm).



(a) Solvent: 0.5 M NaCl (b) Solvent: deionized water

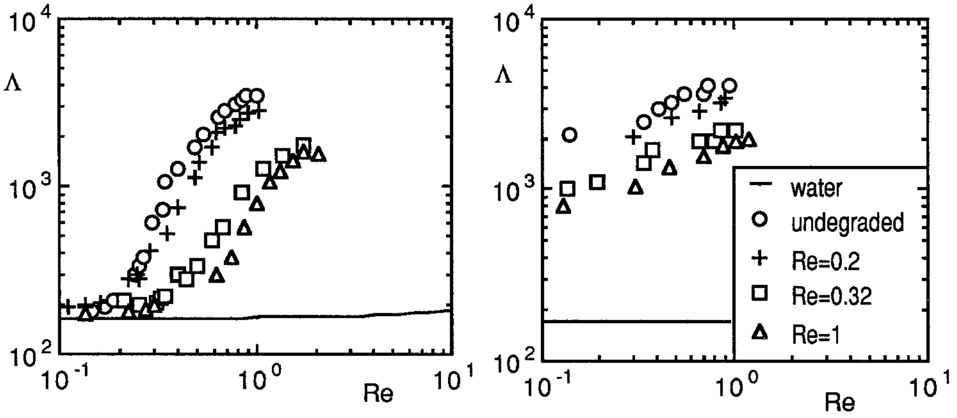
Figure 4. Opposed jets pressure drops of original and degraded 50 ppm HPAA solutions. Number of passes for degraded solution is the maximum for which results are presented in figure 2 (for legend see figure 3).

The same type of experiments discussed above were performed using a disordered packing of spheres with 0.27 mm in diameter. The variation of resistance coefficient with number of passes is presented in figure 5, whereas the resistance coefficients of the degraded solutions are shown in figure 6. The trends observed in figures 5 and 6 are similar to those reported for the larger particles. The degradation extent strongly depends on whether the extension thickening regime has been reached.



(a) Solvent: 0.5 M NaCl (b) Solvent: deionized water

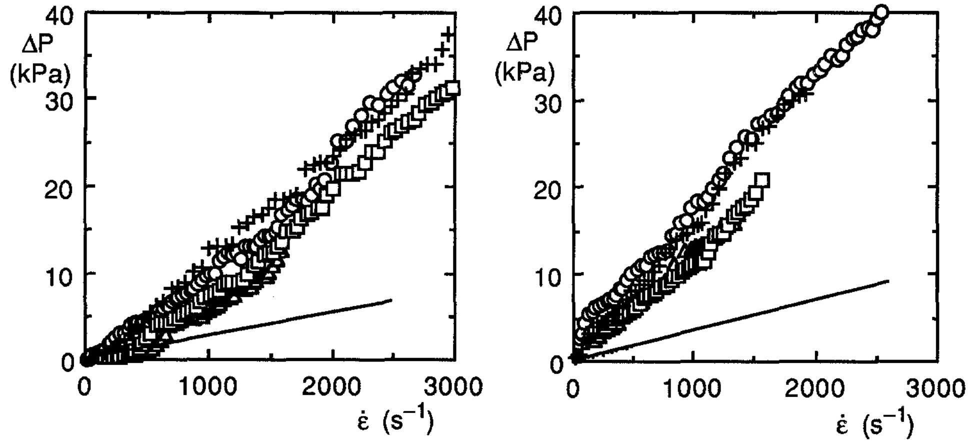
Figure 5. Decrease in resistance coefficient during porous media degradation of 50 ppm HPAA solutions at constant Reynolds number (d=0.27 mm).



(a) Solvent: 0.5 M NaCl (b) Solvent: deionized water

Figure 6. Resistance coefficients of original and degraded 50 ppm HPAA solutions. Number of passes for degraded solution is the maximum for which results are presented in figure 5 (d=0.27 mm).

Our results show that, under the conditions analyzed, the extent of ultimate degradation increases as the particle diameter increases. This can be gathered by comparing the opposed jets results of the degraded solutions (figures 4 and 7), from which it is evident that the apparent elongational viscosity of the solutions degraded in the bed with the larger particles are generally lower than those degraded in the small particle medium. The reason for this trend is not completely clear. However, it is possible that the flow fields at the pore level are being affected by the non-Newtonian nature of the solution in such a manner that they significantly differ for the two different particle sizes. Different flow fields would lead to different distribution of strain rates and, therefore, a different degradation behavior.



(a) Solvent: 0.5 M NaCl (b) Solvent: deionized water

Figure 7. Opposed jets pressure drops of original and degraded 50 ppm HPAA solutions. Number of passes for degraded solution is the maximum for which results are presented in figure 5 (for legend see figure 6).

Conclusions

The flow-induced degradation behavior of HPAA molecules in porous media flows varies with the ionic environment. For solutions in deionized water, in which the HPAA behaves as a semi-rigid polymer, an appreciable degree of viscosification is observed in all the range of Reynolds numbers explored and there is always appreciable degradation. For solutions in 0.5 M NaCl, in which the HPAA behaves as a flexible polymer, extension thickening occurs after an onset flow rate. Irrespective of particle size, degradation only sets in when extension thickening occurs. However, the extent of degradation increases with an increase in particle size.

References

1. Rodríguez S, Romero C, Sargenti ML, Müller AJ, Sáez AE, Odell JA (1993) J Non-Newt Fluid Mech 49:63
2. Maerker JM (1975) SPE J August:311
3. Farinato RS, Yen WS (1987) J Appl Polym Sci 33:2353
4. James DF, McLaren DR (1975) J Fluid Mech 70:733
5. Käser F, Keller RJ (1980) J Eng Mech Div ASCE EM3:525
6. Chauveteau G (1986) in: Glass JE (ed) Water-soluble polymers. ACS, Washington (Advances in chemistry series, vol 213)
7. Haas R, Kulicke W-M (1985) in: Gampert B (ed) The influence of polymer additives on velocity and temperature fields. Springer, Berlin
8. Müller AJ, Medina LI, Pérez-Martín O, Rodríguez S, Romero C, Sargenti ML, Sáez AE (1993) Appl Mech Rev 46:S63
9. Sáez AE, Müller AJ, Odell JA (1994) Colloid Polym Sci 272:1224
10. Müller AJ, Odell JA, Keller A (1988) J Non-Newt Fluid Mech 30:99
11. Odell JA, Müller AJ, Narh KA, Keller A (1990) Macromolecules 23:3092
12. Tatham JP, Carrington S, Odell JA, Gamboa AC, Müller AJ, Sáez AE (1995) J Rheol 39: 961
13. Kulicke W-M, Haas R (1984) Ind Eng.Chem Fundam 23:306
14. Odell JA, Müller AJ, Keller A (1988) Polymer 29: 1179
15. Odell JA, Keller A, Müller AJ (1992) Colloid Polym Sci 270: 307