Viscous Fingering in Polymer Solutions

M. Kawaguchi *

Department of Chemistry for Materials, Faculty of Engineering, Mie University,

1515 Kamihama, Tsu, Mie, 514-8507 Japan

SUMMARY: Characteristics of viscous fingering patterns in polymer solutions were investigated by radially pushing air in a radial Hele-Shaw cell containing hydroxypropyl methyl cellulose (HPMC) solutions. Low and high molecular weight HPMC samples were used. An increase in molecular weight easily yielded chain entanglements, which led to a strong shear thinning and an increase in elasticity. For the low molecular weight HPMC solutions, only the dense-branching patterns were observed over the entire injection pressure range. When isopropyl alcohol was added into the HPMC solutions, leading to less elasticity, the pattern was tip-splitting one, which is observed for Newtonian fluids. On the other hand, for the high molecular weight HPMC solutions, the resulting patterns showed a systematic change from dense-branching to skewering patterns through tip-splitting patterns as the injection pressure increased. The measured tip velocity was compared with the modified Darcy's law, but the coincidence is poor. The velocity corrected by the displaced area ratio provided a good linear relation.

Introduction

Viscous fingering phenomena is a kind of pattern formation far from equilibrium pattern formation and its pattern is developed by an instability during the displacement of a more viscous fluid by a much less viscous one in a Hele-Shaw cell [1-3]. The observed patterns are similar to those found in processes such as crystal growth and electrochemical deposition of metals. These processes can be described in terms of the evolution of a moving boundary that is controlled by transport processes on one or both sides of the boundary. In the most simple cases, the transport process can be expressed by Laplace equations.

The basic transport equation in the viscous fingering is given by Darcy's law

$$v = \frac{b^2}{12\eta}\nabla p \qquad (1)$$

where v is the finger tip velocity, b is the cell gap, η is the viscosity of the more viscous fluid, and ∇p is the pressure gradient. Equation 1 is held for Newtonian fluids [1-3]. However, for non-Newtonian fluids, such as polymeric solutions, we may attempt to replace the constant viscosity η by the shear dependent viscosity η_{eff} and to find a modified Darcy's law:

 CCC 1022-1360/00/$ 17.50+.50/0

$$v = \frac{b^2}{12\eta_{eff}} \nabla p \qquad (2)$$

Some viscous fingering experiments have been performed in polymer solutions, leading to dendrite pattern, fractal structures, and fracture like fingers [4-10]. Furthermore, the variety of experimental observations have led to some theoretical works to account for some features observed in the experiments [11-13]. However, understanding of the viscous fingering in such polymeric systems is not complete since they show a number of different non-Newtonian properties. In this paper, the viscous fingering in a radial Hele-Shaw cell filled with aqueous solutions of hydroxypropyl methyl cellulose (HPMC) will be discussed in terms of pattern morphology and finger tip velocity.

Experimental Section

Two HPMC samples supplied by Shin-Etsu Chemical company were purified by the method described previously [7-10]. Their molecular weights were determined to be 2.51×10^5 g/mol and 7.40×10^5 g/mol by the intrinsic viscosity measurement and the respective HPMC samples were designed by HPMC-1 and HPMC-2. The shear viscosities of the respective samples were determined at 25 °C by a strain controlled rheometer attached with a cone and plate geometry.

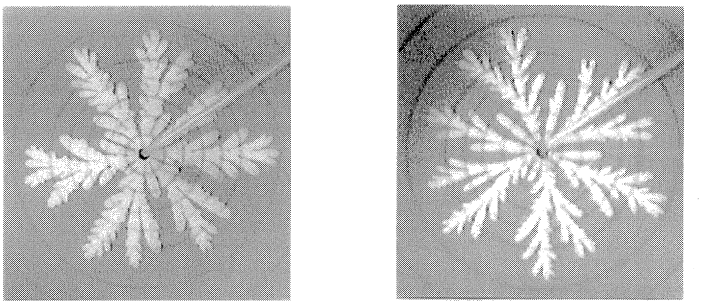
A radial Hele-Shaw cell was made by using two plane glass sheets ($0.8 \times 50 \times 35$ cm^3) with a silicon wafer spacer of 0.05 cm thickness clamped in between the plates [7, 8]. The sample was injected to form a 10 cm sample radius and air was injected. The fingering experiments were performed at 25 °C. The generated finger patterns were recorded with a CCD camera-recorder system and their analysis was performed by a Himawari digital analyzer.

Results and Discussion

Pattern Morphology

The 1.5 g / 100 ml HPMC-1 solution displayed weak shear thinning behavior above a shear rate of 50 s^{-1} and the zero shear viscosity was determined to be 0.140 Pa·s. Its fingering pattern is classified as a dense-branching pattern, irrespective of the injection pressure. Some

typical obtained patterns are shown in Fig. 1. When the concentration of HPMC was less than the overlapping concentration of HPMC, 0.19 g / 100 ml, the patterns were similar to the tip-splitting ones observed for Newtonian fluids [8], suggesting that the dense-branching pattern is due to the viscoelastic properties resulting from the chain entanglements.



a b

Fig. 1. Viscous fingering patterns of the 1.5 g / 100 ml HPMC-1 solutions at various injection pressure of 2.0 (a) and 5.0 (b) kPa. The concentric circles in the photographs have the radii of 1, 2, 3, 5, 7, and 9 cm.

Addition of isopropyl alcohol (IPA) to the 1.5 g / 100 ml HPMC-1 solution leads to a poor solvent quality, since IPA is a non-solvent for HPMC. IPA content was changed from 3 to 10 vol. %. Thus, with an increase in the IPA content it can be expected that a HPMC chain make a more compact form and its elastic property should become weaker, leading to morphological transition of the viscous fingering pattern from dense-branching pattern to tip-splitting one [7]. The transition was opposite to the computer simulation result of Liang, who took account of changes in the surface tension [14]. The discrepancy would be due to a decrease in elastic properties rather than the surface tension of the HPMC solution with an increase in IPA content.

An increase in the molecular weight of HPMC can easily yield chain entanglements, which lead to a higher elastic modulus and a shear thinning onset at a lower shear rate. The 0.6 g / 100 ml HPMC-2 solution showed stronger shear thinning behavior beyond the shear rate of 10 s^{-1} and its shear viscosity at the shear rate of 10^3 s^{-1} was less than quarter of the zero shear viscosity of 0.193 Pa·s. Fig. 2 shows typical patterns of the 0.6 g / 100 ml HPMC-2 solution as a function of the injection pressure. At 2.0 kPa a dense-branching pattern is observed. It was found that the tips of the faster growing fingers advance with an oscillation. The oscillation advancement is never periodic. At 3.0 kPa the side-branches are suppressed and the growth of the finger is basically classified as tip-splitting, where the finger tip is less

rounded. At 4.0 kPa the fingers are wider and the finger tip is more rounded than at 3.0 kPa. At 5.0 kPa the finger growth is quite different from the usual tip-splitting pattern: the growing tip is broad, flattening, and around the middle of flattening tip a new bumping is formed. We will denote the finger growth as a skewering pattern.

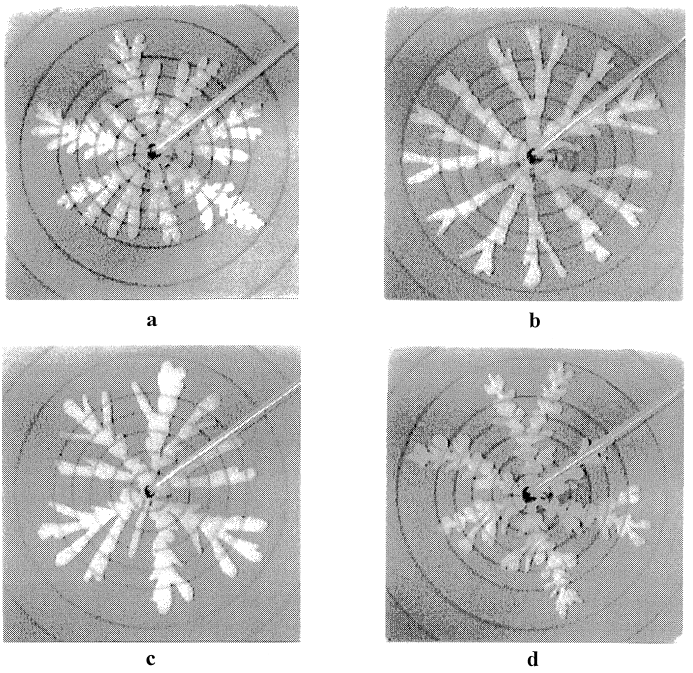


Fig. 2. Viscous fingering patterns of the 0.6 g / 100 ml HPMC-2 solutions at various injection pressure of 2.0 (a), 3.0 (b), 4.0 (c), and 5.0 (d) kPa. The concentric circles in the photographs have the radii of 1, 2, 3, 5, 7, and 9 cm.

Similar morphological pattern changes in the fingering pattern as a function of injection pressure were observed for the 0.4 and 0.5 g / 100 ml HPMC-2 solutions. However, such changes seem to be continuous rather than evidence of sharp "dense-branching to splitting" and "splitting to skewering" morphology transitions [8]. Moreover, when the temperature is raised, the morphology transition is observed at higher injection pressure [15].

Finger Velocity

In order to understand changes in the patterns of the HPMC solutions, we defined a finger tip velocity by the ratio of a given distance from the center of the cell to the time necessary for

the outermost parts of the finger to reach the distance. The distance was nearly proportional to the time up to around the distance of 5 cm and above the distance the plot was gradually and upwardly deviated from the straight line. In this study we focus on the average finger tip velocity, v determined from the slope of the initial straight line.

As mentioned above, we should consider a typical strain shear rate imposed on the HPMC-2 solutions for the respective injection pressure. Such a shear rate can be defined by the ratio of the finger tip velocity to half of the plate spacing [16]. The imposed shear rates were obtained to be 10-500 s^{-1} for the measured tip velocities. For such imposed shear rates, the values of η_{eff} could be interpolated from the plots of the shear viscosities as a function of the shear rate. Using such values of η_{eff}, we plot the v values for the HPMC-2 solutions as a function of $(\nabla p / \eta_{eff})$ in Fig. 3, where ∇p is the ratio of the applied pressure to the distance between finger tip and the sample radius. The v value increases with an increase in $\nabla p / \eta_{eff}$ but it is quite positively deviated from the slope of equation 2, which is indicated by a dashed line in Fig. 3. The discrepancy may be attributed to not taking the displaced area ratio by the injected air into account [9, 10]. The product of the displaced area ratio and the v value is defined as v_{cor} and the data points of v_{cor} fit well on the dashed line as shown in Fig. 3.

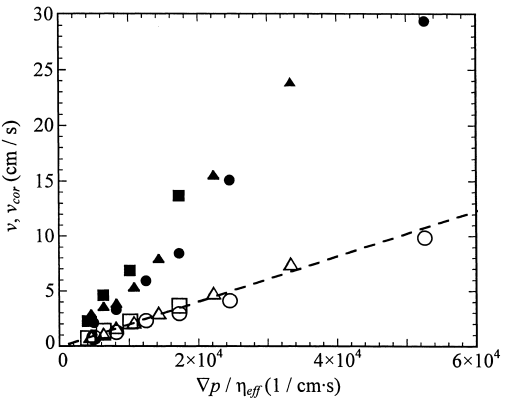


Fig. 3. Plots of v (filled symbols) and v_{cor} (open symbols) values for the HPMC-2 solutions as a function of $\nabla p / \eta_{eff}$; circles = 0.4 g / 100 ml, triangles = 0.5 g / 100 ml, squares = 0.6 g / 100 ml.

Conclusions

The low molecular weight HPMC solutions showed a dense branching pattern, irrespective of the injection pressure and below the overlapping concentration the resulting patterns were tip-

splitting ones observed for Newtonian fluids. On the other hand, the high molecular weight HPMC solutions exhibited continuous changes in the morphology of the finger pattern from dense-branching to skewering pattern via tip-splitting with an increase in the injection pressure. Their tip velocities corrected by the displaced area ratio were proportional to the ratio of the pressure gradient to the shear dependent viscosity of HPMC solution, irrespective of the pattern morphology.

References

1. T. Vicsek, *Fractal Growth Phenomena*, World Scientific, Singapore 1992, p. 302
2. P. Meakin, *Fractals, Scaling, and Growth far from Equilibrium*, Cambridge University Press, Cambridge, 1998, p. 44
3. K. V. McCloud, J. V. Maher, *Phys. Rep.* **260**, 139 (1995)
4. H. Zhao, J. V. Maher, *Phys. Rev. A* **45**, R8328 (1992); *Phys. Rev. E* **47**, 4278 (1993)
5. D. Bonn, H. Kellay, M. Ben Amar, J. Meunier, *Phys. Rev. Lett.* **75**, 2132 (1995); *Physica A* **220**, 60 (1995)
6. D. Bonn, J. Meunier, *Phys. Rev. Lett.* **79**, 2662 (1997)
7. K. Makino, M. Kawaguchi, K. Aoyama, T. Kato, *Phys Fluids* **7**, 455 (1995)
8. M. Kawaguchi, K. Makino, T. Kato, *Physica D* **109**, 325 (1997)
9. M. Kawaguchi, A. Shibata, K. Shimomoto, T. Kato *Phys. Rev. E* **58**, 785 (1998)
10. M. Kawaguchi, S. Shimomoto, A. Shibata, T. Kato, *Chaos* **9**, 323 (1999)
11. L. Kondic, P. Palffy-Muhoray, M. J. Shelley, *Phys. Rev. E* **54**, R4536 (1996)
12. L. Kondic, M. J. Shelley, P. Palffy-Muhoray, *Phys. Rev. Lett.* **80**, 1433 (1998)
13. E. C. Poire, M. B. Amar, *Phys. Rev. Lett.* **81**, 2048 (1998)
14. S. Liang, *Phys. Rev. A* **33**, 2663 (1986)
15. M. Kawaguchi, K. Makino, T. Kato, *Kagaku Kogaku Ronbunshu* **25**, 516 (1999)
16. H. Van Damme, E. Lamaie, in: *Disorder and Fracture*, J. C. Charnet, S. Roux and E. Guyon (Eds.), Plenum, New York 1986, p. 83