Rheological Behavior of Ultrahigh Molecular Weight Polyethylene Semidilute Solutions. I. Solvent Effect*

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Synopsis

The rheological behavior of ultrahigh molecular weight polyethylene (UHMWPE) semidilute solutions with different solvents has been studied. In a temperature range of 150–185°C, the viscosity of a UHMWPE semidilute solution with paraffin oil as solvent (soln 1) is more temperature-independent and viscosity-stable than that with decalin as solvent (soln 2). Usually the reduction of the molecular entanglement density in solution causes a rapid reduction in viscosity. Apparently soln 1 has a different entanglement density compared with soln 2. The activation energy of UHMWPE semidilute solutions changes with both shear stress and shear rate. The regressive equations for both solutions in between E_σ and σ or $E_{\dot\gamma}$ and $\dot\gamma$ have been obtained from a least-squares method. Finally, there is a discontinuity in the non-Newtonian flow region of η vs. $\dot\gamma^{1/2}$ curve, no matter which temperature or solvent was used. The discontinuity occurs at a shear rate of about 70 s^{-1}, where a transformation from a qualitative change in entanglement in the solution takes place.

INTRODUCTION

Ultrahigh molecular weight polyethylene (UHMWPE) is a prerequisite for the preparation of polyethylene (PE) filaments with high strength and high modulus. There are several techniques available for producing high strength and high modulus PE filaments; gel spinning and hot drawing are the most significant ones. The most widely accepted solvents for preparing UHMWPE solutions are decalin[1] and paraffin oil.[2,3]

This paper presents a study concerning the rheological behavior of UHMWPE semidilute solutions (5 wt % PE) with decalin and paraffin oil as solvents. The flow curves of the two solutions were investigated by a capilliary rheometer.

MATERIALS AND METHODS

The linear UHMWPE powder ($\overline{M}_w = 1.59 \times 10^6$) used in the study was a commercial product from Beijing Second Chemicals Co., Beijing, China. The solvents used were laboratory reagent grade decalin (Shanghai Chemical Reagents Co., Shanghai) and laboratory reagent paraffin oil (Shanghai Oil Refining Co., Shanghai). 2,6-Di-*t*-butyl, 4-methyl-cresol was used as an antiox-

idant. The following procedures were adopted for the preparation of UHMWPE semidilute solutions; UHMWPE powder (5 wt %), antioxidant (0.1 wt %), and solvent were added at room temperature. With stirring, the suspension was heated to either 150°C in decalin or 170°C in the case of paraffin oil and kept at these temperatures for 2 h. A vacuum (below 10 torr) was applied to the solution for over 4 h for degassing. The solution was subsequently allowed to form a gel by slowly cooling to room temperature. The resulting gel was cut into small pieces prior to rheological measurements.

The rheological study was performed in an Instron Model 3211 capillary rheometer with a diameter of 1.53 mm, a length of 101.66 mm, and an entrance angle of 120°C.

RESULTS AND DISCUSSION

Viscosity vs. shear rate curves with decalin and paraffin oil as solvents at 150–185°C are shown in Figures 1–3. These two solutions showed different flow behavior at 150 and 185°C, two temperatures which are in the normal range of spinning. UHMWPE powder is fully dissolved in decalin at 150°C. The solution with paraffin oil as solvent had a lower shear viscosity compared with the decalin solution shown in Figure 1. At higher temperatures, however, the situation was quite different. For example, at 185°C the shear viscosity of decalin solution was significantly reduced compared to the paraffin oil solution shown in Figure 3. According to Ferry,[4] a polymeric fluid is composed of a homogeneous entanglement network. The difference between the entanglement density in solutions may affect the flow behavior of the solutions. Increasing the entanglement density increases the intermolecular action between the molecular segments, and results in poorer flow behavior and lower stability. Judging from the flow curves shown in Figures 1–3, it may be deduced that the decalin solution contains a higher entanglement density at the lower temperature of 150°C and lower entanglement density at the higher
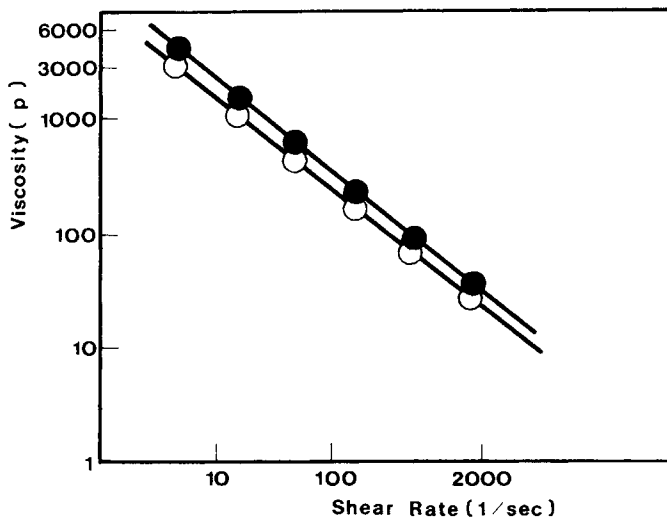

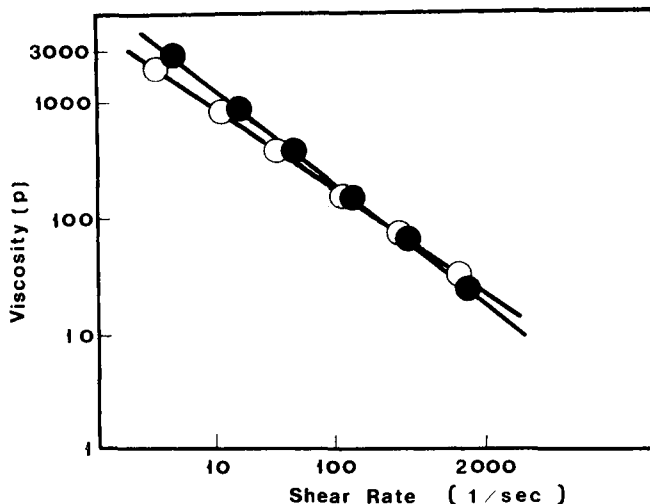Fig. 1.   Viscosity vs. shear rate (5 wt % UHMWPE, 150°C): (●) decalin; (○) paraffin oil.

Fig. 2.   Viscosity vs. shear rate (5 wt % UHMWPE, 170°C): (●) decalin; (○) paraffin oil.

temperature of 185°C when compared to the paraffin oil solution. Furthermore, the viscous flow and the entanglement structure of the decalin solution are much more temperature-dependent. Since its activation energy is higher (shown in Table I). Its entanglement density becomes lower at the higher temperature of 185°C. It is obvious that the flow curves of these two solutions would intersect at a temperature between 150 and 185°C, such as 170°C shown in Figure 2.

It has already been known that viscosity is a function of temperature, as shown in Figures 4 and 5, since viscous flow is a diffusion process. In order to study the flow stability of non-Newtonian fluids, the viscosity–temperature function should be considered. The viscosity–temperature function can be
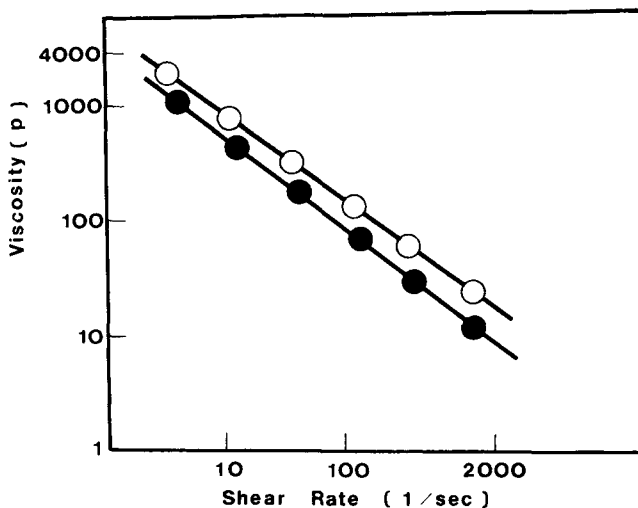

Fig. 3.   Viscosity vs. shear rate (5 wt % UHMWPE, 185°C): (●) decalin; (○) paraffin oil.

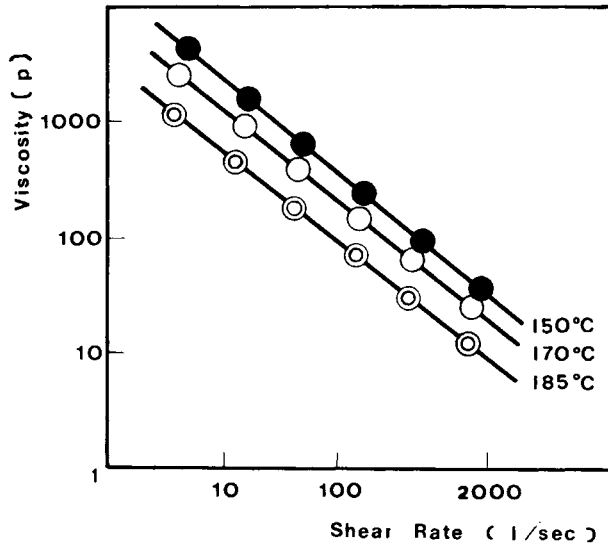| Decalin			Paraffin oil	
$E_{\dot\gamma}$ (kcal/mol)	$\dot\gamma$ (s^{-1})		$E_{\dot\gamma}$ (kcal/mol)	$\dot\gamma$ (s^{-1})
14.42–11.33	7.39–148		9.03–3.85	7.39–403

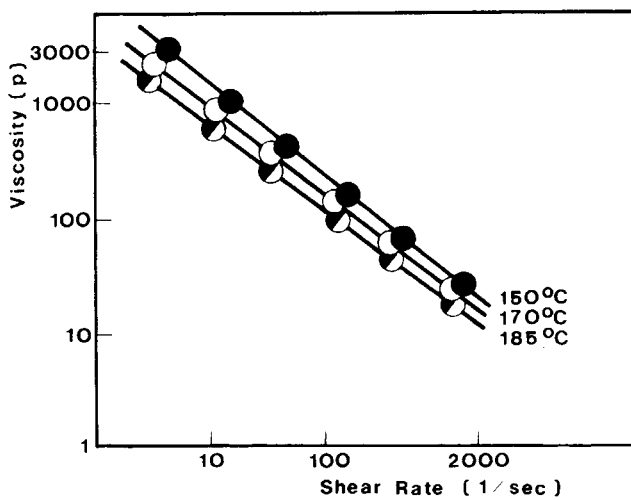Fig. 4. The effect of temperature on the flow curve (5 wt % UHMWPE, decalin).

Fig. 5. The effect of temperature on the flow curve (5 wt % UHMWPE, paraffin oil).
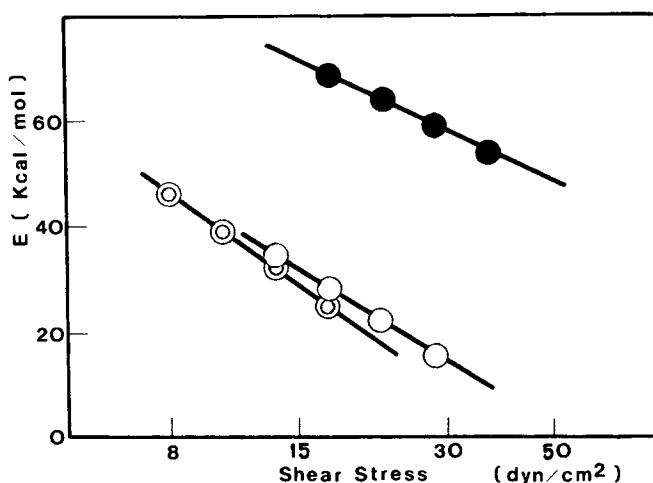
Fig. 6. E vs. shear stress (5 wt % UHMWPE): (●) decalin; (○) paraffin oil; ((⊚)) 1 wt % Al stearate, paraffin oil.

studied either at constant shear stress or at constant shear rate. Many investigators pointed out that it is possible to express the temperature dependence of viscous flow in terms of an Arrenius-type equation involving the activation energies at constant shear stress and at constant shear rate.

Figures 6 and 7 show that in both solutions the activation energies changed with a change shear stress and shear rate. The regression equations for both solutions for the activation energy and shear stress (or shear rate) from the least-squares method are as follows:
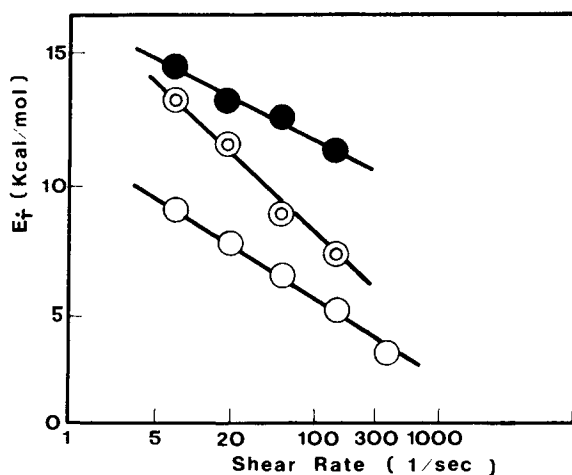

Fig. 7. $E_{\dot{\gamma}}$ vs. shear rate (5 wt % UHMWPE): (●) decalin; (○) paraffin oil; ((⊚)) 1 wt % Al stearate, paraffin oil.

For decalin solutions:

$$E_\sigma = 258.77 - 19.51 \ln \sigma \quad \text{kcal/mol}, \quad r = 1$$

$$\left(\sigma = 17{,}000\text{–}36{,}500 \text{ dyn/cm}^2 \right)$$

$$E_{\dot\gamma} = 16.30 - 0.98 \ln \dot\gamma \quad \text{kcal/mol}, \quad r = 0.99$$

$$\left(\dot\gamma = 7\text{–}150 \text{ s}^{-1} \right)$$

For paraffin oil solutions:

$$E = 271.30 - 25.02 \ln \sigma \quad \text{kcal/mol}, \quad r = 1$$

$$\left(\sigma = 13{,}000\text{–}28{,}500 \text{ dyn/cm}^2 \right)$$

$$E = 11.69 - 1.29 \ln \dot\gamma \quad \text{kcal/mol}, \quad r = 1$$

$$\left(\dot\gamma = 7\text{–}410 \text{ s}^{-1} \right)$$

E_σ and $E_{\dot\gamma}$ are the activation energies at constant shear stress σ and at constant shear rate $\dot\gamma$, respectively. It can be seen that the activation energies changed not only with the change of shear rate but with shear stress as well. This behavior is quite different from other polymer fluids such as poly(ethylene terephthalate) so that E remains almost unchanged when the shear stress increases.

Figure 8 shows the relation between the viscosity and the square root of shear rate of a UHMWPE semidilute solution. It is interesting to note that there is a discontinuity in η vs. $\dot\gamma^{1/2}$, as was observed in the case of poly(vinyl alcohol) solutions.[5] Discontinuity is basically at a shear rate of about 70 s^{-1}, independent of solvent and concentration. This means that the UHMWPE
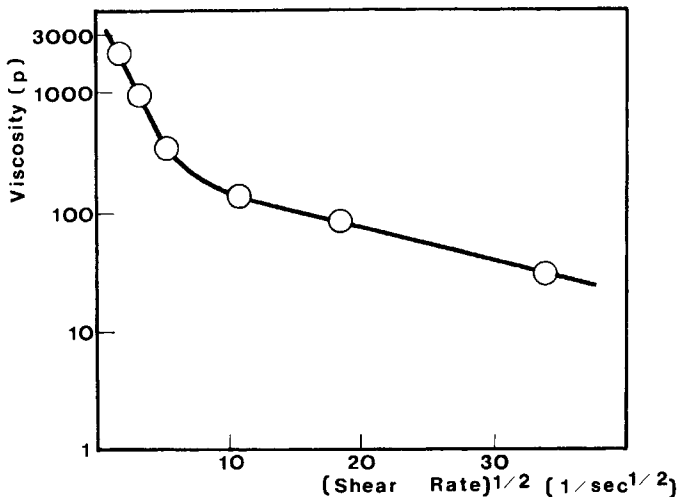

Fig. 8. Viscosity vs. shear rate for 5 wt % UHMWPE in decalin at 170°C.

semidilute solutions perform a higher degree of structuralization at shear rates below 70 s^{-1}, and a lower degree of structuralization at shear rates above 70 s^{-1}. In view of an entanglement network,[6] the entanglement density of a polymer solution is related to the shear stress when the instantaneous entanglement network reaches a dynamic equilibrium. The structure of a polymer solution changes strikingly as the entanglement density is decreased through destroying part of the entanglements by increasing the shear stress (also the shear rate). When the shear rate reaches about 70 s^{-1}, a transformation from a quantitative change in entanglement takes place, which results in the occurrence of a discontinuity in η vs. $\dot{\gamma}^{1/2}$ curve.

CONCLUSION

UHMWPE semidilute solutions using paraffin oil or decalin as solvents has similar flow behavior to that of a pseudoplastic fluid. The solution with paraffin oil has better flow behavior than with decalin in a temperature range of 150–170°C, but this is reversed in the range of 170–185°C. Also, there is a discontinuity in η vs. $\dot{\gamma}^{1/2}$. Moreover, the activation energies of flow depend not only on the shear rate, but to a greater degree on the shear stress as well. This is quite different from other polymer fluids such as poly(ethylene terephthalate), etc.

References

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