

Viscous Behavior of Ultrahigh Molecular Weight Polyethylene Solution

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ABSTRACT: The viscous behavior of the decalin solution of ultrahigh molecular weight polyethylene (UHMEPE) was studied. The influence of the concentration of polymer as well as the temperature was investigated. The flow curve can be described by the power-law model. The dependence of the viscosity on the temperature can be described by the Arrhenius–Frenkel–Eyring equation. The dependence of viscosity on the concentration can also be described by a power-law correlation. The addition of aluminum stearate increased the activation energy of flow of the solution. The viscosity of UHMWPE solution was decreased at lower concentration and increased at higher concentration of UHMWPE. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 289–293, 1997

Key words: ultrahigh molecular weight polyethylene; solution; viscosity; temperature; concentration; aluminum stearate

INTRODUCTION

Ultrahigh molecular polyethylene (UHMWPE) fiber has high modulus and high strength. Manufacturing of UHMWPE fibers is usually through gel spinning and hot drawing.^{1–7} There are many studies in the literature concerning the gel-spinning process as well as the drawing process.^{8–13} In the process of gel spinning, UHMWPE is dissolved in a suitable solvent, and the solution is extruded through the spinneret. The UHMWPE solution at lower temperature (<95°C) may become gel and thus is termed as gel spinning. However, it is actually a kind of solution spinning. The formation of UHMWPE fiber is affected by many factors. In the course of fiber formation, the rheological properties of the solution affect the viscoelastic behavior of the extrudate, and hence, affect

the mechanical properties of the resulting fiber. However, very few reports in the literature can be found to be related to the rheological behavior of the UHMWPE solution. Zachariades et al.^{14,15} studied the viscoelastic behavior of UHMWPE gels. As for UHMWPE solutions, there are only two articles on this subject. Zhang et al.¹⁶ reported the effect of solvent on the viscosity of UHMWPE solutions, while Chen et al.¹⁷ reported the effect of the addition of aluminum stearate on the viscous behavior.

The focus of this study is the viscous behavior of the UHMWPE solution. There are two ways to control the viscosity of the solution. One is through temperature, which not only affects the viscosity itself, but also affects the diffusion rate of the solute as well as the solubility of the polymers. The other way is through the change of the composition of the solution. Both effects are studied in this project. The results are summarized into empirical correlations. In so doing, we hope these results can be useful for analyzing the spinning flow in the gel-spinning process in order to obtain suitable spinning conditions.

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EXPERIMENTAL

Materials

Ultrahigh molecular weight polyethylene (UHMWPE) of $M_w = 4.5 \times 10^6$ was obtained from Formosa Plastics Co., Taiwan. Decalin and the antioxidant 2,6-di-*t*-butyl,4-methyl cresol (BHT) was obtained from Ferak, Germany. Aluminum stearate was obtained from Hayashi Chemicals Co., Japan. All materials were used as received.

Preparation of UHMEPE Solution

Powder of UHMWPE was add into decalin according to the specified concentration. Aluminum stearate was added when necessary. The liquid mixture was slowly stirred at 150°C for 5 h. To prevent the degradation of the polymer, 1 wt % of BHT was also added to decalin, and the flask was purged with nitrogen.

Viscosity Measurement

The viscosity of the UHMWPE/decalin solution was taken using a Brookfield viscometer (model LVDV1+) with three spindles to cover different ranges of viscosity. The measurement was performed in a thermal barrel. Because the polymeric flow was in the annulus of two concentric cylinders, which is known as the Couette flow, the rotating speed of the spindle and the measured load from the viscometer was corrected to obtained the strain rate and the stress.

RESULTS AND DISCUSSION

Flow Curve

The flow curves of UHMWPE in decalin at five temperatures are shown in Figure 1. We can see that these data points are forming straight lines. This trend is in agreement with the results of Zhang et al.^{16,17} Due to the limitation of the viscometer, the range of the strain rate is between 0.1 and 100 s^{-1} , which is less than the range of Zhang et al. (5–2000 s^{-1}). Even at low strain rate, however, we can see that the data are still falling on a straight line. This straight line suggests that the viscosity η and the strain rate $\dot{\gamma}$ can be described by the power law:

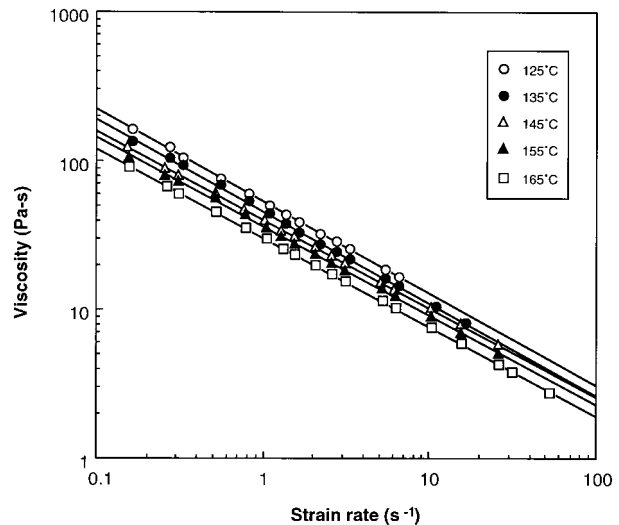


Figure 1 Flow curves of 2 wt % UHMWPE decalin solution at five temperatures. Solid lines are based on power law fitted results: ○—125°C, ●—135°C, △—145°C, ▲—155°C, □—165°C.

$$\eta = m\dot{\gamma}^{n-1} \quad (1)$$

where m is the consistency, and n is known as the flow index.¹⁸ We fitted these data with eq. (1) by linear regression to obtain m and n . The results were summarized in Table I. The fitted lines are also plotted in Figure 1.

Effect of Temperature on Viscosity

In the literature, the viscosity is known to depend on the temperature according to the Arrhenius–Frenkel–Eyring (AFE) equation¹⁸:

$$m = m_0 \exp(\Delta E/RT) \quad (2)$$

where ΔE is the activation energy of flow, and R is the gas constant. This dependence was confirmed in Figure 2, where the consistency m was plotted vs. the reciprocal of the temperature. Although the consistency is not viscosity, we may treat it as the viscosity at strain rate 1 s^{-1} . As shown in Table I, the flow index is ranging from 0.380 to 0.402 without clear dependence on the temperature. This suggests that the non-Newtonian behavior of this UHMWPE solution changed

Table I Consistency and Flow Index for Fitting Viscosity of 2 wt % of UHMWPE Decalin Solution

T (°C)	m	n
125	53.2	0.381
135	46.2	0.380
145	40.4	0.404
155	36.3	0.402
165	30.4	0.401

little in the temperature range between 125 and 165°C. Thus, the viscosities at other strain rates are also following the AFE formula. Based on eq. (2), a master curve can be obtained by multiplying a factor to the viscosity, as follows:

$$\eta' = \eta \frac{m_s}{m_T} \quad (3)$$

where m_s is the m at a reference temperature, which is 125°C in this case, and m_T is the m at temperature T . The master curves of all concentrations were plotted in Figure 3. As shown in Figure 3, all the master curves are approximately straight lines. Each line is corresponding to a concentration. These straight lines are approximately parallel to each other, suggesting that the activation energy ΔE is not strongly affected by the concentration.

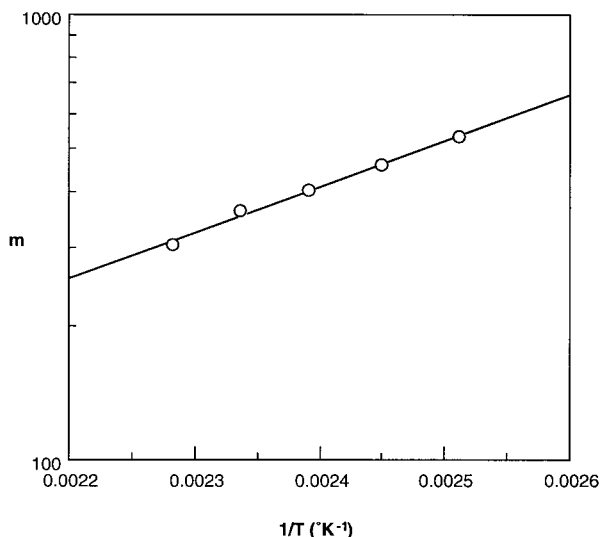


Figure 2 Dependence of consistency of 2 wt % UHMWPE decalin solution on temperature. The solid line is based on the AFE equation.

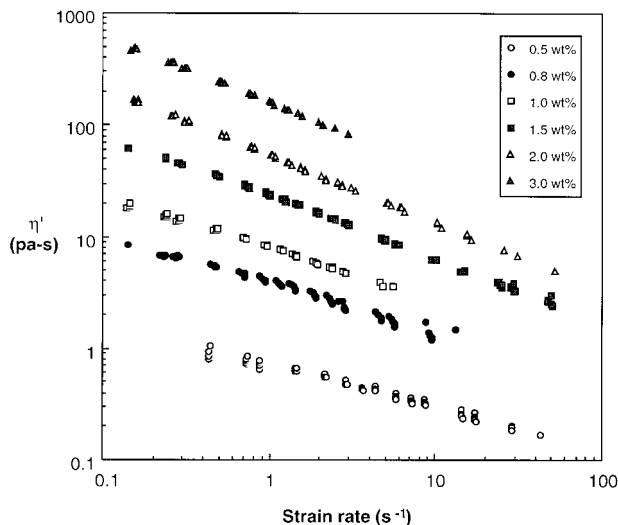


Figure 3 Viscosities of UHMWPE decalin solution of six different concentrations. ○—0.5 wt %, ●—0.8 wt %, □—1.0 wt %, ■—1.5 wt %, △—2.0 wt %, ▲—3.0 wt %.

Effect of Concentration on Viscosity

This indicates that concentration is affecting the viscosity of the UHMWPE solution. In the textbook, the viscosity of a polymer solution is known empirically to be dependent on the concentration in a power-law fashion¹⁸:

$$\eta = Kc^\alpha \quad (4)$$

where c is the concentration, and α is a constant. Actually, the factor K should also include the effect of molecular weight, but in this study we did not have sample of other molecular weight, and hence, the effect was hidden in K . Although this equation is originally for the zero-shear viscosity η_0 , we found that it is also applicable to other strain rates. As shown in Figure 4, the consistencies of each temperature is falling on a line vs. the concentration. By taking linear regression on the consistency against both the temperature and the concentration, we arrived the following correlation:

$$m = kc^\alpha \exp(\Delta E/RT). \quad (5)$$

The fitted values of k , α , and ΔE are tabulated in Table II. In addition, the values of n are plotted in Figure 5 vs. the concentration. We can see that the value of n decreased with the increase of the concentration. This indicates

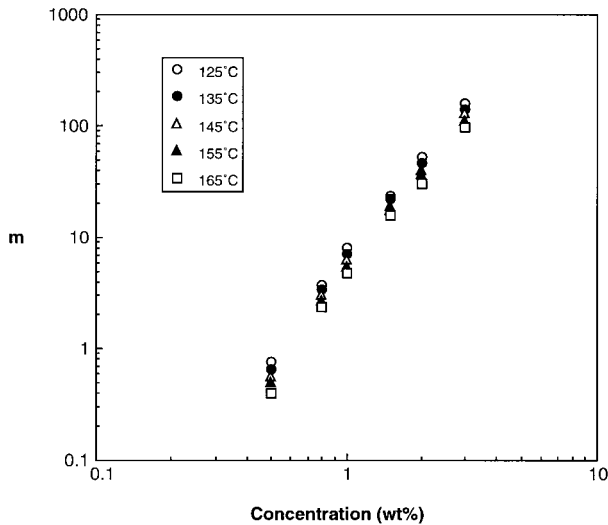


Figure 4 Dependence of consistency of UHMWPE decalin solution on the concentration at different temperatures. ○—125°C, ●—135°C, △—145°C, ▲—155°C, □—165°C.

that the solution is more non-Newtonian for more concentrated solution. However, the decrease in n is leveled off when the concentration is higher than 1.5 wt %.

Effect of Addition of Aluminum Stearate on Viscosity

Aluminum stearate is added to the UHMWPE solution as a lubricant for fiber spinning. As indicated by Smook and Pennings,¹⁰ the presence of aluminum stearate can reduce the spinning instability and, hence, increase the take-up speed. Its addition can affect the viscosity of the solution. In order to compare the viscosities at different temperature and concentration, we shifted the temperature based on eq. (5) as follows:

Table II Results of Linear Regression on Consistency Against Both Concentration and 1/T

Concentration of Aluminum Stearate (wt %)	k	α	ΔE (kJ/mol)
0	0.2560	2.977	18.54
1	0.0016	2.670	36.06

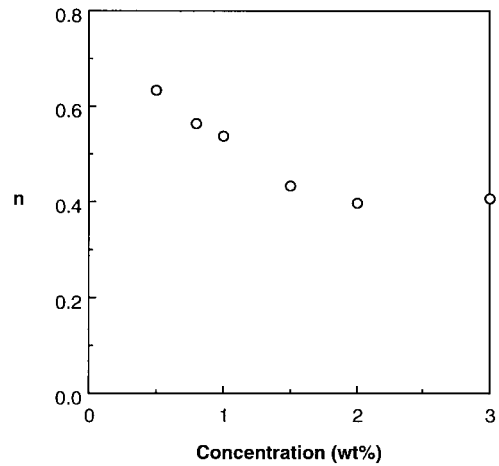


Figure 5 Dependence of flow index of UHMWPE decalin solution on the concentration.

$$\frac{1}{T'} = \frac{1}{T} + \frac{R\alpha}{\Delta E} \ln(c). \tag{6}$$

The master curves of the consistency were plotted vs. the shifted reciprocal of temperature in Figure 6. We can see from Figure 6 that these two master curves intersect at $1/T' = 0.0025$ ($T' = 400$ K). This indicates that at lower concentration, the addition of aluminum stearate can reduce the viscosity. On the other hand, at higher concentration, addition of aluminum stearate can increase the viscosity. At 125°C and 1 wt % UHM-

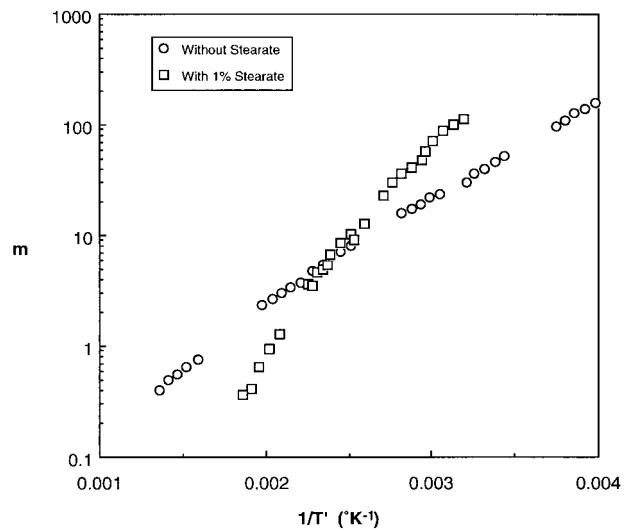


Figure 6 Master curves of consistency of UHMWPE decalin solution with respect to the shifted reciprocal of temperature. ○—without aluminum stearate; □—with 1 wt % aluminum stearate.

WPE, addition of aluminum stearate does not much affect the viscosity.

The slopes of these two master curves are different. The curve with aluminum stearate added is steeper than the other curve. In Table II, we can see that the activation energy of the solution with 1 wt % stearate is about twice of that of the solution without stearate. It is known that the activation energy of flow in a poor solvent is higher than in a good solvent.¹⁸ Therefore, the addition of stearate makes decalin "poorer" for UHMWPE. In a poor solvent the polymer-polymer interaction is stronger than the polymer-solvent interaction. When the concentration is low, the occurrence of entanglement is less due to the smaller radius of gyration of the polymer chain. Therefore, the viscosity of UHMWPE solution with stearate is lower than the solution without stearate at low concentrations. However, the entanglement is stronger due to stronger polymer-polymer interaction in a poor solvent. Thus, ΔE is higher in the solution with stearate. This is also the reason why the viscosity at higher concentration is higher for the solution with stearate than the solution without stearate.

CONCLUSION

The viscosity of UHMWPE decalin solution is in general following a power law correlation with respect to the strain rate. The consistency m depends on the temperature following the Arrhenius-Frenkel-Eyring formula. The flow index n is less affected by the temperature.

The dependence of viscosity of UHMWPE solution is following a power-law correlation. The flow index decrease from 0.63 at 0.5 wt % to about 0.4 at 3 wt %. This is reasonable, because the solution becomes more non-Newtonian at higher concentration.

The addition of aluminum stearate changes both the temperature and the concentration de-

pendency of the viscosity. The stearate causes the reduction of the viscosity for dilute solution, while increasing the viscosity at more concentrated solution.

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