Rheological Behavior of Ultrahigh Molecular Weight Polyethylene Semidilute Solutions. II. Effect of Aluminium Stearate*

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Synopsis

The effect of aluminium stearate on the rheological behavior of ultra-high molecular weight polyethylene (UHMWPE) semidilute solutions with paraffin oil as the solvent has been investigated. Adding aluminium stearate to paraffin oil can prevent the spinning solution from adhering to the pipe or screw, greatly improving the flow behavior of UHMWPE solutions. The geometric sizes of spinnerette hole, such as length–diameter ratio L/D and entrance angle of a capillary, also affect the flow behavior of the spinning solution. The calculated first normal stress difference $\sigma_{11} - \sigma_{22}$ and the Bagley-end correction e from experimental data show that the elastic effect on spinning solutions in flow is quite large, although the shear rate is below 20 s^{-1}.

INTRODUCTION

In the past decade the preparation of the ultrahigh strength and ultrahigh modulus polyethylene filaments has been achieved by a variety of processes: solid state extrusion under high pressure,[1] crystallization from a solution in extensional flow, referred to as "surface growth,"[2] and gel spinning/hot drawing.[3-5] Among them, the latter is the most effective and economical technique for producing ultrahigh molecular weight polyethylene (UHMWPE) filaments. There are many reports dealing with experimental and theoretical studies on UHMWPE filaments produced by gel spinning and hot drawing, mainly on the relationship between structure, draw ratio, and mechanical properties. However, articles on rheological studies of UHMWPE solutions are still lacking. Pennings et al.[6] pointed out that the manufacturing of UHMWPE filaments with a strength of 3 GPa necessitates the take-up speed to be less than 10 m/min during extrusion of a 5 wt % solution of UHMWPE in paraffin oil. The addition of 1 wt % aluminium stearate to paraffin oil has a surprisingly great effect on the strength–take-up speed relationship. In such cases, the take-up speed is as high as 270 m/min and the strength level will still remain on the order of 3 GPa. However, they did not deal with the effect of aluminium–stearate on rheological behavior of the solution.

In the preceding paper,[7] we have studied the rheological behavior of UHMWPE semidilute solutions with decalin and paraffin oil as solvents. The aim of this paper is to declose the effect of Al stearate as an auxiliary on the rheological behavior of the solution.

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MATERIALS AND METHODS

A linear UHMWPE powder ($\overline{M}_w = 1.59 \times 10^6$) obtained from Beijing 2nd Chemicals Company, Beijing, China was used. The solvent was paraffin oil (laboratory reagent, Shanghai Oil Refinement Inc., Shanghai) and 2,6-di-*t*-butyl, 4-methyl cresol (laboratory reagent, Shanghai Auxiliary Inc., Shanghai) was used as an antioxidant and Al stearate as an auxiliary. The procedures of preparing UHMWPE semidilute solutions and measuring viscous flow curves with an Instron Model 3211 capillary rheometer have been discussed previously.[7]

To simulate the actual spinning process, some of the rheological studies were performed with a 3-L stirring vessel, a tube for the solution flowing, and a one-hole spinnerette (shown in Fig. 1, length-diameter ratio $L/D = 2$–15, entrance angle = 6–60°). The homogeneous flow was pushed out of the spinnerette by compressed air under different pressures. The mass of solution coming out of the spinnerette was weighed. With different L/D and entrance angle spinnerettes, a series of pressure versus mass flow rate curves was obtained. The data for the flow curve can be obtained by the Bagley-end correction.[8] The calculations are as follows:

$$\dot{\gamma}_N = \frac{4W/(td)}{\pi R^3} \tag{1}$$

$$n = \frac{d \ln p}{d \ln \dot{\gamma}_N} \tag{2}$$

$$\dot{\gamma} = \frac{3n + 1}{4n} \dot{\gamma}_N \tag{3}$$

$$P = 2\sigma L/R + 2\sigma(C + \gamma_e/2) \tag{4}$$

$\dot{\gamma}_N$ is the maximum shear rate at the wall of the capillary, W is the mass flow coming out of the capillary at time t, and d is the specific gravity of the solution. σ denotes shear stress and $\dot{\gamma}$ the shear rate. P is the total pressure difference between a point upstream in the reservoir and the exit of the capillary. L and R are the length and radius of the capillary, respectively. C is the Couette correction and γ_e the recoverable shear strain in the Bagley-end correction: $e = C + \gamma_e/2$. Furthermore, the relationship between the first normal stress difference ($\sigma_{11} - \sigma_{22}$) and γ_e can be written as

$$\sigma_{11} - \sigma_{22} = \sigma \times \gamma_e \tag{5}$$

RESULTS AND DISCUSSION

In the dissolution process of UHMWPE with paraffin oil, as the temperature gradually rises up to 110°C, the swelling UHMWPE powder aggregates causing difficulty in homogeneous dissolution of UHMWPE. Since the generated aggregates are the results of higher surface energy powders, the addition

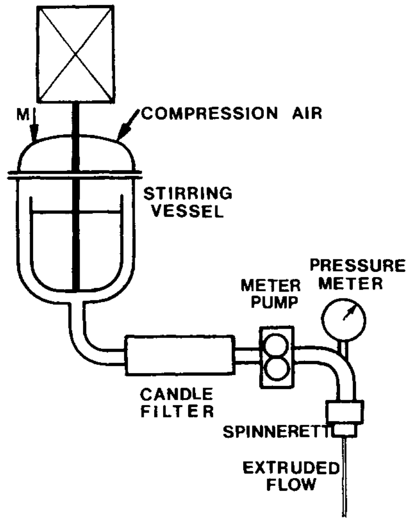

Fig. 1. The scheme of spinning apparatus.

of nonionic surfactants may decrease the surface energy of the nonpolar powders. This has already been demonstrated in our test. Furthermore, Smook and Pennings[9] pointed out that, in the manufacturing of UHMWPE filaments with a strength of less than 1.5 GPa by applying extrudate stretching, the macromolecules at the center of the die are most easily pulled out. These macromolecules are, however, connected to the strongly absorbed, immobile layers alongside the die wall, which guarantees an effective stretching of the entanglement network. However, the relatively low viscosity of the molten state enables macromolecules to slip easily out of an entanglement coupling, after which they immediately recoil. This sudden recoiling of macromolecules may generate elastic turbulence, and the entanglement structure in

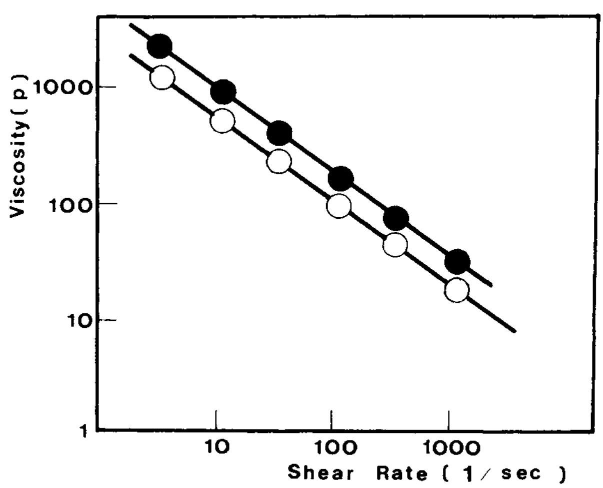

Fig. 2. Viscosity vs. shear rate: (●) without Al stearate; (○) 1 wt % Al stearate; 5 wt % UHMWPE Paraffin oil, 170°C.

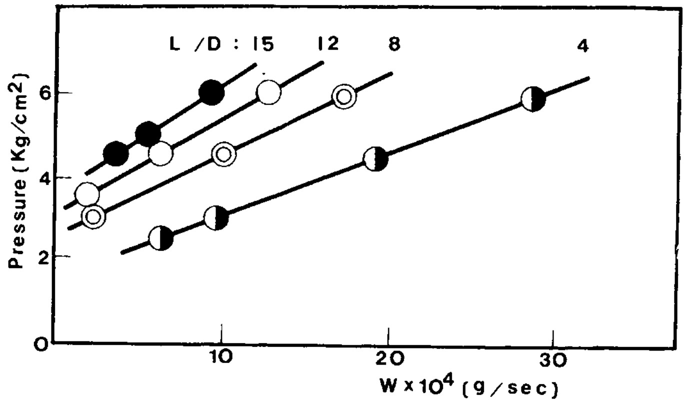

Fig. 3. Pressure vs. mass flow W: 5 wt % UHMWPE + 1 wt % Al stearate, paraffin oil; entrance angle 60°; 170°C.

the quickly spun filaments will be completely disrupted. The presence of Al stearate in the spinning solution makes it possible to produce gel filaments with a higher take-up speed; for example, adding 1 wt % Al stearate into a 5 wt % UHMWPE solution, a take-up speed between 100 and 300 m/min can be achieved. The gelled materials do not adhere at all to the screw; hence, absorption of polyethylene molecules will be strongly reduced by Al stearate. Presumably the metal ions in Al stearate have a strong cohesion with the metal surface of the die. Accordingly, an absorbed Al stearate layer will be formed between the flowing polymer solution and die wall. This will promote a more regular flow of the solution as a result of reduced elastic flow instabilities. Moreover, the viscosity of the solvent will be increased substantially by the addition of Al stearate to the spinning solution. In a more viscous medium the slippage of polyethylene macromolecular chains through entanglements will be inhibited. The flow curves of UHMWPE semidilute solution

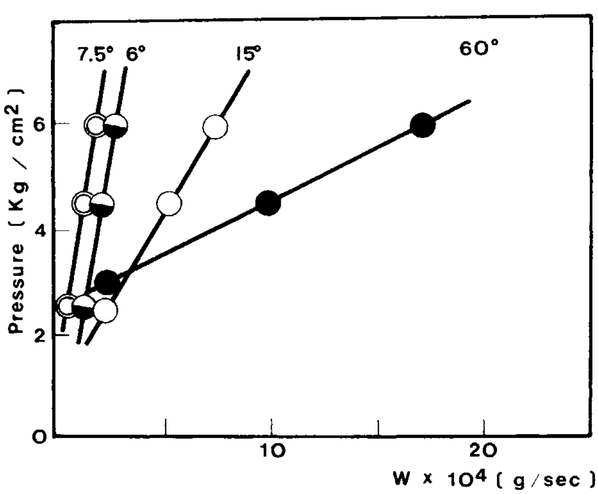

Fig. 4. Pressure vs. mass flow W: 5 wt % UHMWPE + 1 wt % Al stearate, paraffin oil; L/D 8; 170°C.

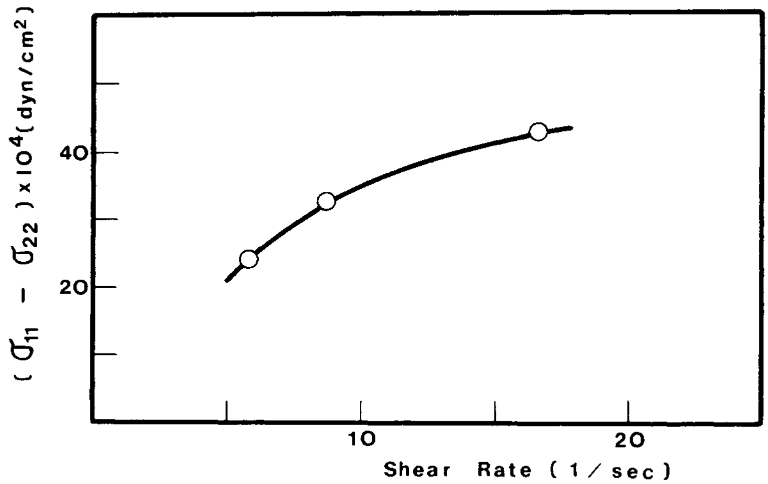

Fig. 5. The first normal stress difference vs. shear rate: 5 wt % UHMWPE + 1 wt % Al stearate, paraffin oil; entrance angle 60°; 170°C.

with and without Al stearate are shown in Figure 2. It is evident that by adding Al stearate the flow behavior of the spinning solution is improved.

The geometric sizes of the spinnerette hole also affect the flow behavior of the spinning solution. An increment in L/D or decrease in the entrance angle of a capillary produces an increased resistance to viscous flow; at the same time it is likely to promote the development macromolecular relaxations so as to restrain the flow process from the elastic turbulence as shown in Figures 3 and 4.

As is well known, a polymer fluid is viscoelastic whereby it stores elastic energy when passing through a pipe. The stored elastic energy is partially dissipated as the fluid enters the tube, where it is completely converted to recoverable elastic energy. Figure 5 gives the $(\sigma_{11} - \sigma_{22})$ vs. shear rate curve for a UHMWPE semidilute solution, determined from capillary die data with the aid of eq. (5). Figure 5 shows that $(\sigma_{11} - \sigma_{22})$ increases with the increment of the shear rate. This is constant with other elastic behavior; for instance, the Weissenberg effect, die swell behavior, and Bagley-end correction (given in Fig. 6). The Bagley-end correction e is composed of two parts, i.e., $e = (P_{exit} + P_{ent})/2$, as both exit pressure (P_{exit}) and entrance pressure (P_{ent}) originate from the elastic effect in the flow of a polymer fluid, and the shear stress σ is a viscous effect. The magnitude of the e value denotes the elestic effect over the viscous effect in the flow of the viscoelastic fluid. The higher the e value, the greater the elastic effect, and, consequently, there is an increase in the elastic unstable flow in the spinning solution, such as in the die swell behavior. It can be seen that the elastic effect on the spinning solution in viscous flow is significantly large even if the shear rate is below 20 s^{-1}.

CONCLUSIONS

The flow curves of UHMWPE semidilute solutions with Al stearate at different temperature and different geometric size (e.g., L/D and entrance

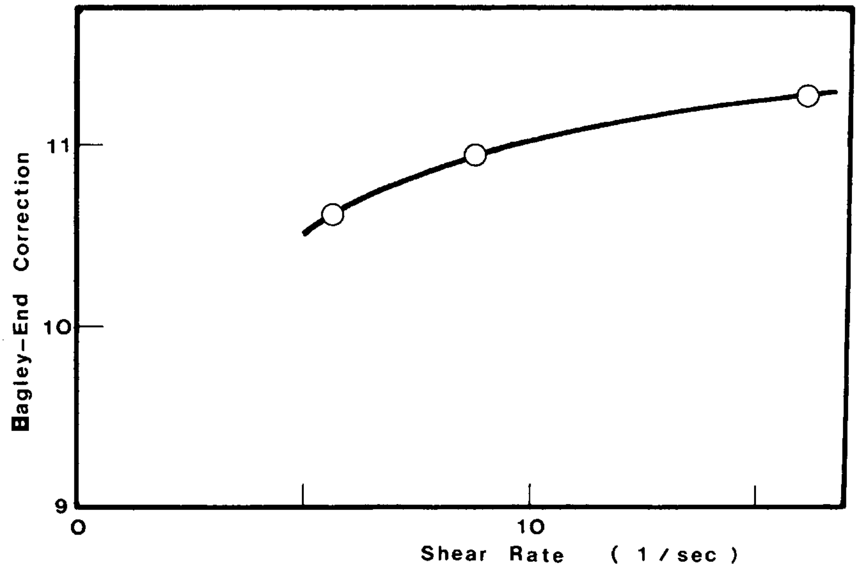

Fig. 6. Bagley-end correction vs. shear rate: 5 wt % UHMWPE Al stearate, paraffin oil at 170°C.

angle of a capillary) of spinnerette holes have been obtained. Adding Al stearate to paraffin oil remarkably improves the rheological behavior of UHMWPE semidilute solution. The L/D value and entrance angle of a capillary also affect the flow stability of the UHMWPE solution. Curves of $(\sigma_{11} - \sigma_{22})$ vs. $\dot{\gamma}$ or e vs. $\dot{\gamma}$ illustrate the elastic effect on the spinning solution in viscous flow even if it is at a low shear rate.

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