Characterization of the Rheological Behavior of UHMWPE Gels Using Parallel Plate Rheometry

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ABSTRACT: The effects of shear flow, temperature, and gel concentration on the rheological behavior of the ultrahigh-molecular-weight polyethylene (UHMWPE) gel in gel spinning process were investigated. The gel point was determined using parallel plate rheometry in rotation mode with controlled stress. Likewise, the flow curves at various temperatures were determined with controlled shear rate from 10^{-2} to 10 s^{-1}. Whereas the shear storage modulus (G') was obtained in oscillation mode with controlled strain from 1 to 100%. The result shows that the gel point of the UHMWPE gel increases with increasing gel concentration. The result from the strain sweep indicates that G' of the gel is 1.5×10^3 Pa, and it exhibits a plateau at low strain, but it is reduced with increasing strain. At low shear rates, for temperatures above gel point, all flow curves exhibit a plateau, then go down with increasing shear rate. Studying contributions from UHMWPE gel concentration, temperature, and shear rate for rheological view, we found that spinning at 6% UHMWPE (MW : 1.4×10^6 g/mol) gel and 140°C gives the best effect on formation of fiber structure. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1009–1016, 1998

Key words: rheological behavior; UHMWPE gel; gel spinning; parallel plate rheometry

INTRODUCTION

The ultrahigh-molecular-weight polyethylene (UHMWPE) fiber employing gel spinning technology[1,2] is an extended chain structure fiber with shish kebabs crystals,[3] which gives high performance. Therefore, how to control rheological behavior in gel spinning process and to obtain an effective structure is important to manufacturing optimum UHMPW fiber. Unfortunately, the structure change and control mechanism of rheological behavior were not investigated in details previously. Therefore, the microstructure control in gel spinning process is a primary purpose to apply rheology.

In previous articles, the UHMWPE fiber is well prepared in consideration of, besides sufficiently high molecular weight, the preparation for spinning dope, solvent, gel concentration, temperature, and stirring are essential. On top of those, the applications of gel spinning and super drawing make possible the high strength fiber with extended chain structure. The solvents used in literature so far include decalin,[4,5] paraffin oil,[5,6] cycloakane,[7] and xylene.[8] The formation of the polyethylene gel is affected by the solvents used. Wu and coworkers[9,10] researched the effects of various solvents on the UHMWPE gel using capillary rheometry and found that the gel prepared with decalin has higher activation energy. On the other hand,

the addition of aluminium stearate can increase spinning speed if paraffin oil is served as solvent. Whereas Matsuo and coworkers[11,12] gave the relationship between molecular weight and optimum concentration, the researched concentration range was 2–10% and investigated the relationship between the fiber formed of various concentrations and super drawing.

The cone–plate rheometry is employed extensively in study of polymer fluids. It is generally used to investigate (1) the rheological behavior of the polymer fluids; (2) the effect of filler added in the polymer; (3) the effect of the blending or copolymer; and (4) the examination on microstructure. Lakdawala and Salovey[13] employed polystyrene and poly(butyl methacrylate)-filled carbon black. Carbon black was added to the copolymer in a toner system, primarily as a pigment, in order to effect printing. In experiment, cone–plate rheometry was used to determine the rheological properties of the polymer filled with carbon black in an attempt to comprehend the effects of carbon black concentration and surface area on the polymer's viscosity and shear rate. Mutel and Kamal[14] investigated the characterization of the rheological behavior of fiber-filled polypropylene melts under steady and oscillatory shear using cone and plate and rotational parallel plate rheometry. Under steady shear conditions, the addition of fibers increases the viscosity, as in all suspensions, and there is a positive correlation between the concentration of fibers and the increase in viscosity. The effect of fibers on the steady shear viscosity at any concentration is higher at low shear rates, and the relative viscosity decreases with increasing shear rate. Jingshua and coworkers[15] utilized cone–plate rheometry to investigate the rheological properties and the crystallization characteristics of low-ethylene-content polypropylene (EPM) with and without Yittrium oxide as a filler.

From the recent research by Zachariades,[16] it is concluded that the UHMWPE gel can not be considered as a true gel. In fact, UHMWPE gel is a pseudophysical gel, which differs from the true gel, especially in behavior relative to viscosity and temperature. The storage modulus of pseudogels decreases with increasing temperature. It is also found in this research that the viscoelastic behavior is closely related to the formation of fiber structure. However, the correlation between the rheological behavior of the UHMWPE gel and fiber structure was rarely reported. Chung and Zachariades[17] founded that not only the viscosity

of pseudogels is distinctly different from that of gel, but the dynamic viscoelastic characteristics of gel is closely affected by temperature and shear stress. Nizomiya and Ferry[18] attributed the viscoelastic behavior of gel to the temporary entanglement of the molecular chains. And such a behavior is caused by the homogeneous network structure formed among the molecular chains.[19] Therefore, the entanglement density of the polymer will affect the flow behavior of the gel, which can be assessed by the flow curves. The increase of entanglement density will lead to increase of intermolecular action and, consequently, to poorer mobility and stability of the polymer. Since such a gel does not flow without external force applied on it, the strain given to determine its viscoelastic characteristics should be small and within the linear–viscoelastic strain range. With this, the breaking of molecular chains of the gel may be avoided, and the characteristics and behavior of the gel may be observed. According to Jo et al.,[20] the definition of the polymer gel is networks of macromolecular imbibed with a liquid. The major structure contributing to the elasticity of the gel is either irreversible chemical crosslinks or reversible physical crosslinks. In the sol–gel transition, a transition from a solution to gel state, the critical point of the phase transition is gel point. According to literature, the gel point could be determined using the following: ball drop method,[21] thermomechanical analysis[20] (TMA), and the differential scanning calorimetry (DSC) method.[20,22] In this article, the gel point is accurately determined from the relationship between viscosity and temperature that is obtained by monitoring rheological characteristics of the gel.

The UHMWPE fiber is a high-performance fiber by using gel spinning. The performance of the fiber is obviously affected by the forming conditions of gel. Therefore, it is essential to control process conditions in order to obtain the desired forming structure of the gel spinning. The process parameters could be considered gel concentration, temperature, pressure, and filler content. And the major parameters in this experiment were gel concentration, temperature, and shear rate. The experiment was so designed to observe the rheological behavior of the gel under shear rate, using parallel plate rheometry. The control mode options provided by the rheometry are the rotation and the oscillation modes. The shear rate was controlled to determine the flow curves, whereas strain sweep was controlled to determine shear storage modulus (G'). Furthermore, the relation-

ship between viscosity and temperature was also obtained in an attempt to determine the gel point by controlling shear stress in a cooling process.

EXPERIMENTAL

The UHMWPE powder (USI Far Eastern Co., LTD; MW : 1.4×10^6 g/mol) was used in this experiment, and the gel with concentrations of 2, 4, 6, and 7% respectively, was prepared using decalin as solvent. In addition, the Di-t-butyl-p-cresol of 0.5 wt % (base to the polymer) was added as antioxidant. The solutions were stirred at 150°C for 3 h under nitrogen atmosphere until the powder was completed dissolved and the solution was clear.

The rheological behavior was determined using parallel plate rheometry model Paar Physica US200. The measuring plate used was model MP30 ($r = 25$ mm; gap = 1 mm), and a solvent trap system was utilized to avoid error from solvent evaporation. The gel point was determined in rotation mode with shear stress controlled at 100 Pa and temperature ranging from 140 to 60°C. The relationship between viscosity of gel and temperature was determined using a cooling process. The flow curves were obtained in rotation mode by plotting viscosity or shear stress versus shear rate in various gel concentrations (2, 4, 6, and 7%) at temperatures of 80, 100, 120, 140, and 160°C, respectively, with shear rate ranging from 10^{-2} to 10 s^{-1}. The correlation between shear storage modulus (G') and strain sweep was determined in oscillation mode with strain controlled from 1 to 100% and frequency at 2 Hz.

RESULTS AND DISCUSSIONS

The UHMWPE gel is the thermoreversible gel belonging, in general, to the physical aggregation networks in Flory's classification, which is thermoreversible, and crosslinks are formed by physical interactions.[23] Viscoelastic properties change dramatically during the gelation process of a polymer solution, as follows: the system is liquid-like before crosslinking starts and remains a liquid till the viscosity becomes infinite, at the moment, which is called the gel point. The gel point of UHMWPE gel is defined as transition from a solution to gel state of the UHMWPE. As the temperature of gel is lower than gel point, a phase separation will happen, and a surplus solvent will
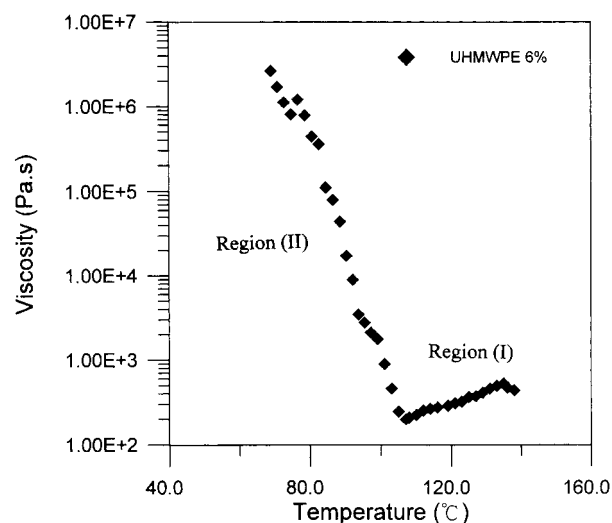
Figure 1 The relationship between viscosity and temperature for 6% UHMWPE gel at a cooling rate of −2°C/min.

be separated. Therefore, the concentration of UHMWPE solution was lower than that in the gel. With this, it is therefore intended in this experiment to determine gel point using a cooling process. The technology used to determine rheological behavior is employed to determine gel point. Figure 1 depicts the viscosity versus temperature for the UHMWPE gel of concentration of 6%. The results were obtained in rotation mode at a cooling rate of −2°C/min and controlled stress at 100 Pa. From Figure 1, it is found that the viscosity of UHMWPE gel first drops and then rises, with decreasing temperature. The drop in the earlier stage could be explained as the effect of orientation change from the application of stress. That is to say, the molecular chains of gel were arrayed in a manner to line up with the shear stress field, and the resistance to flow was therefore reduced. Since the contribution from this effect is greater than that from the temperature decrease effect, the viscosity of gel decreased with respect to time in the gel state. However, as temperature went down to 106.5°C, there appeared a distinct critical point of viscosity. That is to say, the UHMWPE molecular chain in gel at this temperature began to crystallize and formed a cloud texture aggregation. Because molecular weight of the UHMWPE is extremely high, entangled molecular chains easily form tiny domains, which are with arrangement similar to that found in crystalline structure; besides the phase separation also occurs, and the viscosity rises abruptly. The phase tran-
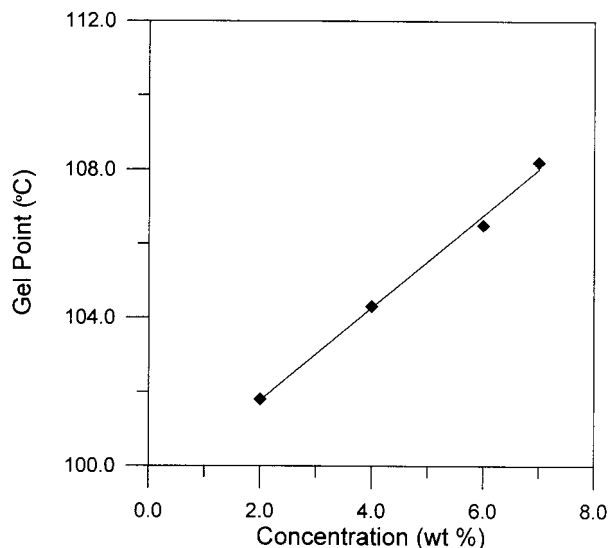
**Figure 2**   The relationship between the gel points and various UHMWPE gel concentrations.

sition point can therefore be defined as a gel point. From the curve shown in Figure 1, it is clear that there are 2 regions, as follows: region (I) at high temperature, where shear-thinning is observed; and region (II), where viscosity rises abruptly, owing to phase separation and formation of domains. The relationship between gel points and various gel concentrations is shown in Figure 2. It is observed that gel point increases with increasing gel concentration. This is owing to the fact that more concentrated gel tends to form more crystals, which contributes to such an increase with gel point. This phenomenon explains that increasing polymer content will be accompanied by an increase of number of entangled molecular chains, which will increase interaction force between molecular. Under constant shear stress, the gel point of higher concentration tends to shift upward. It is further observed in Figure 2 for concentration between 2 to 7% that gel point has a linear relationship with gel concentration.

The viscoelastic behavior of UHMWPE gel could be investigated in oscillation mode. In the experiment, the UHMWPE gel of concentrations 2, 4, 6, and 7% were tested at temperatures 120, 140, and 160°C, respectively. Because the test temperatures were all higher than the gel point, the UHMWPE solution was thus tested in the gel state. The relationship between strain sweep of 6% UHMMPE gel and G' at various temperature is shown in Figure 3. From this figure, it is ob-

served that G' remains a plateau at low strain, though at various temperatures, then it drops dramatically with increasing strain. While at low strain, the value of constant G' is 1.5×10^3 Pa approximately at 140°C, which is close to that obtained by Chiu et al.[22] A distinct critical point appears as the strain reaches 45%. When the strain is lower than 45%, G' does not change distinctly because the molecular chains of gel are arrayed in orientation due to the application of shear stress. As the strain increases to 45%, where the critical point is located, the orientation of molecular chains appear to reach maximal extent, and a physical crosslink interaction force is formed at this point. Further increase of strain will eventually pull the molecular chains out of the entangled region and the molecular chains will begin, consequently, to slide. Due to this, the crystalline region begins to be destroyed, and a dramatic decrease of G' thus happens. As the temperature is 140°C, the G' obtained is higher than those obtained at 120 and 160°C, respectively. The reason is that the gel, being subject to shear stress, forms a shish kebab structure due to the stress-induced crystallization.[24] While the temperature is 120°C, since the crystals were not formed completely, the G' was therefore lower. As temperature increased to 140°C, the perfect crystals were formed due to the higher energy. The G' obtained at this temperature was therefore the maximal value. Further up to 160°C, since the temperature was higher than the melting point of the crystal (147°C), the crystallized domains were
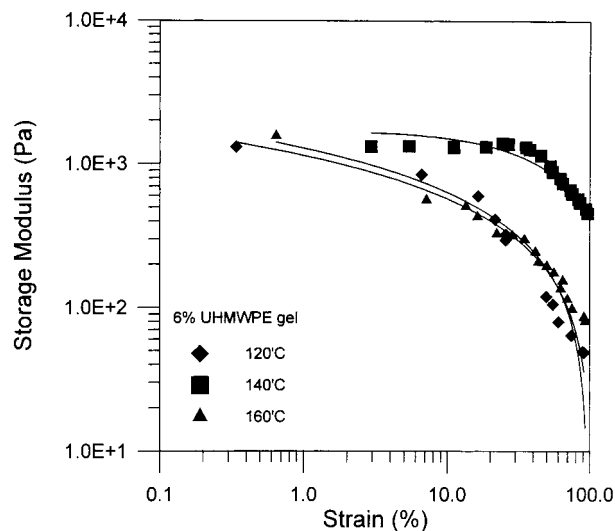
Figure 3   Strain sweep for 6% UHMWPE gel at various temperatures and 2 Hz.
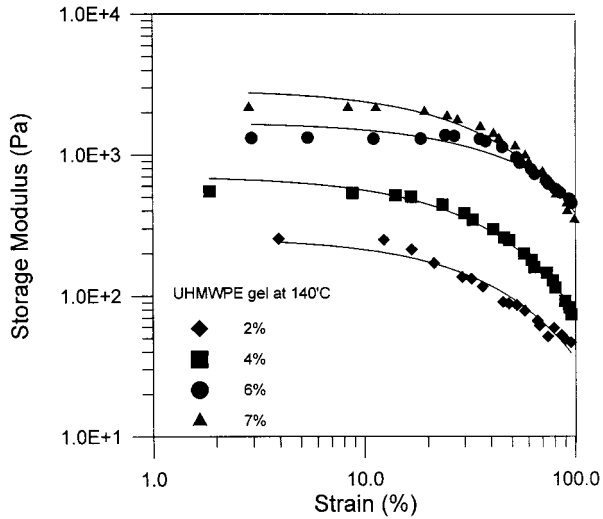
Figure 4 Strain sweep of UHMWPE gel for various concentrations at 140°C and 2 Hz.

destroyed, and the G' decreased instead. Figure 4 shows relationship between shear storage modulus and strain for the UHMWPE gel of various concentrations at 140°C. It is observed that the G' increases with increasing gel concentration, and the critical point shift to higher strain ranges. The highly concentrated gel possesses higher G' because more domains, and more crystals form. In addition, the phenomenon that the critical point tends to increase with increasing strain reveals a fact that the gel possesses more entangled crystals within the molecular chains of gel. And, as a result, the molecular chains can not be easily pulled out the entangled region, and the constant G' region thus tends to go up with increasing strain.

The effects of temperature, gel concentration, and shear rate on the viscosity and shear stress of the UHMWPE gel are illustrated in Figures 5 to 10. Figure 5 shows the flow curves of shear rate and viscosity for 6% UHMWPE gel at temperatures 100, 120, 140, and 160°C, respectively. It is shown that viscosity decreases with increasing shear rate at all curves. However, the linear decrease of viscosity with shear rate observed under 100°C is different from other curves. In fact, 100°C is lower than gel point, and a phase separation has already happened at this temperature. And a turbid texture on the outlook also appears, which suggests a non-gel state. At this state, the structure of gel is not subject to change due to the application of shear stress, and that is a linear relationship that is observed. Furthermore, the

viscosity at this temperature is lower than those under other temperatures. For temperatures that are higher than 120°C, the UHMWPE solution all appear to be in a gel state since they are all above gel point. Therefore, all curves feature the characteristics of shear-thinning fluid, which is the rheological behavior of a pseduoplastic fluid. A critical point at shear rate of 1 s^{-1} is further discovered. At lower shear rates (<1 s^{-1}), the viscosity independence of the shear rate, but viscosity is reduced dramatically once shear rate is greater than this critical point. The reason is that, prior to critical point, the molecular chains of gel is subject to shear stress and undergoes orientation. As shear rate reaches 1 s^{-1}, the orientated structure of molecular chains has been formed; therefore, the resistance to flow is reduced, and the viscosity is also reduced accordingly. It is also observed that viscosity decreases with increasing temperature, but the critical point does not shift distinctly with temperature. Such a finding indicates that there is not obvious relationship between the orientated structure and temperature.

The relationship between shear stress and shear rate for 6% UHMWPE gel is depicted in Figure 6. From this figure, it is found that shear stress only increases slightly with increasing shear rate at 100°C. This indicates that no large amount of deformation and structural change has occurred. At a temperature up to 120°C or above, a peak appears at 1 s^{-1}. Such a critical point is identical to that in Figure 5. Prior to critical
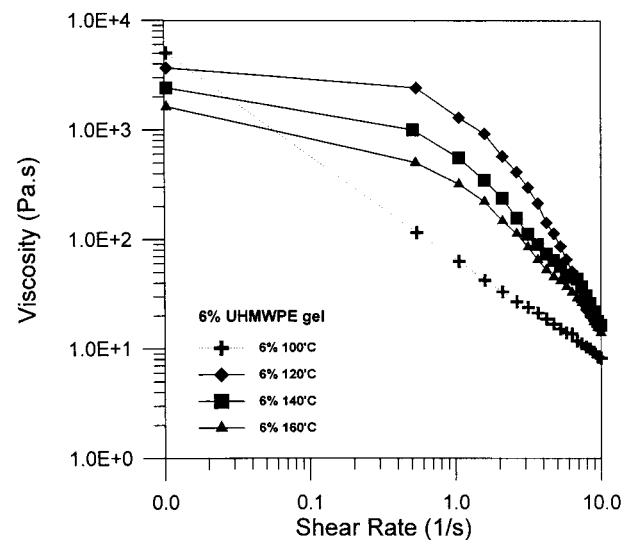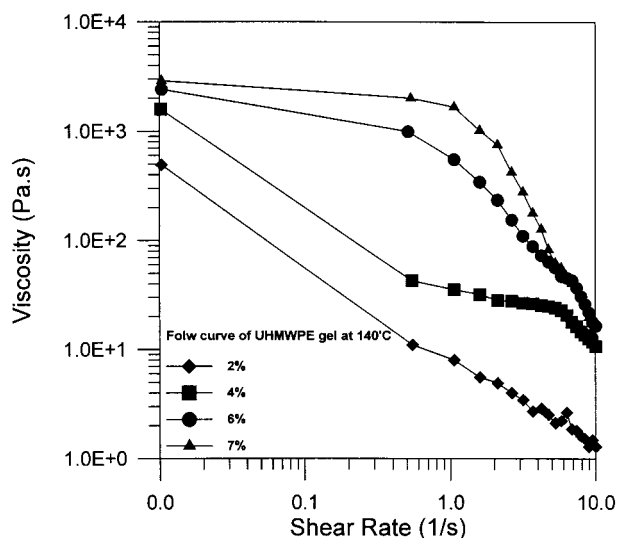

Figure 5 The flow curves of shear rate and viscosity for 6% UHMWPE gel at various temperatures.
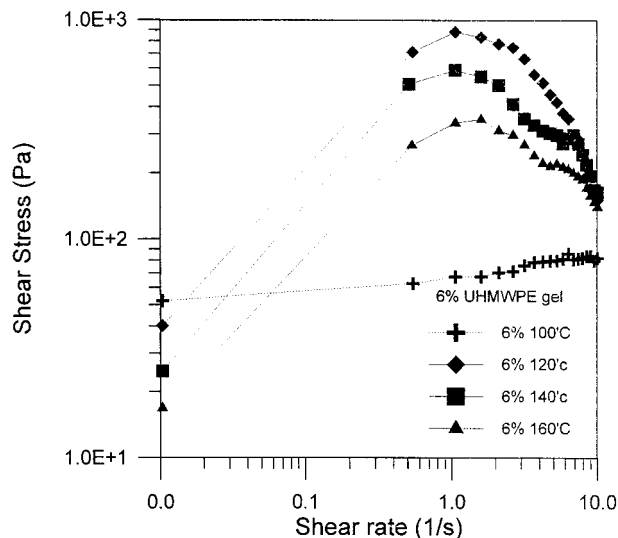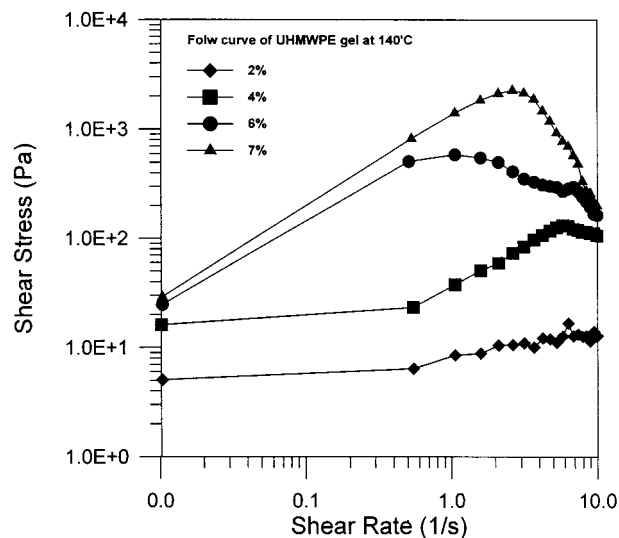
Figure 6 The flow curves of shear rate and shear stress for 6% UHMWPE gel at various temperatures.

Figure 8 The flow curves of shear rate and shear stress for UHMWPE gel at various concentrations and 140°C.

point, a resistance to flow is produced because formation of orientated structure in molecular chains is in process. Later, since the orientated structure has been formed completely, the resistance to flow decreases obviously with increasing shear rate. Further investigation reveals that as test temperature increases, the shear stress reduces obviously as viscosity reduces. Figure 7 shows flow curves of gel of various concentrations for viscosity and shear rate at 140°C. It is shown that all curves feature the characteristics of a pseduoplastic fluid, in which the viscosity de-

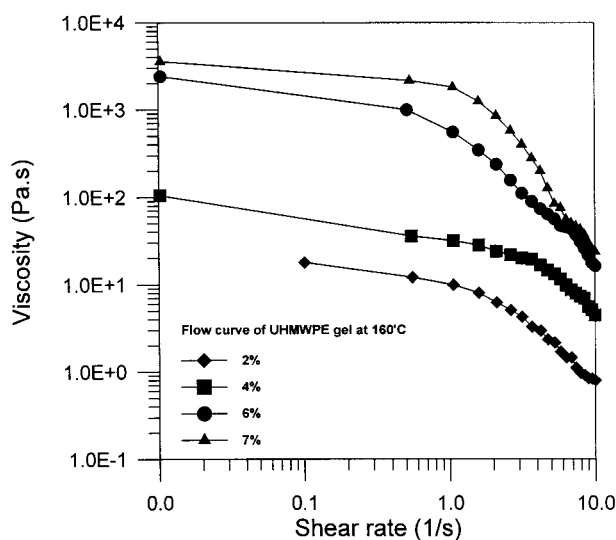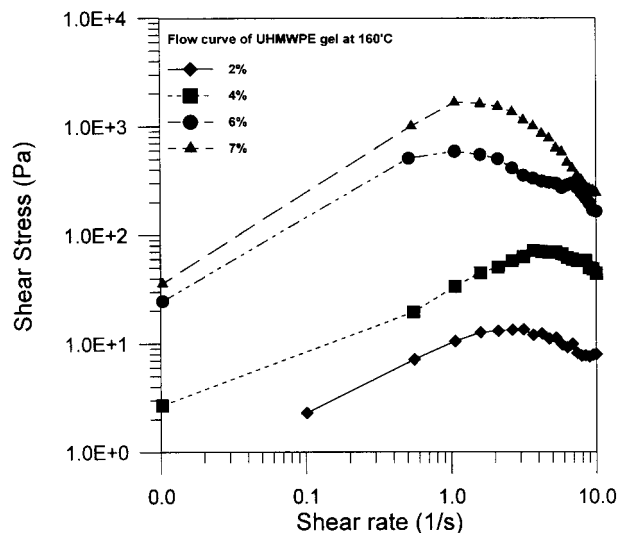**Figure 7** The flow curves of shear rate and viscosity for UHMWPE gel at various concentrations and 140°C.

creases with increasing shear rate. As the UHMWPE gel concentration is 2%, the structure of the molecular chains changes little during the rearrangement process due to the low concentration. Therefore, the flow curve at this concentration appears to be a linear line. As the gel concentration increases, viscosity also increases. In particular, at a concentration of 6%, viscosity remains constant at low shear rates. A critical point appears at shear rate of 1 s^{-1}. And the viscosity is reduced dramatically, while the shear rates are higher than the critical point. Figure 8 depicts the relationship between shear stress and shear rate for UHMWPE gel of various concentrations at 140°C. It is also shown that the resistance to flow increases with an increasing gel concentration. A critical point resulting from orientated structure also appears at about 1 s^{-1}. Figures 9 and 10 illustrate flow curves for the UHMWPE gel of various concentrations at 160°C. It is shown that at this temperature, which is higher than melting point of the crystal, all flow curves display the same characteristics. According to the curves, the viscosity of various concentrations all remain constant when subject to lower shear rate, that is, prior to the critical point. While the shear rate is higher, the critical point and the viscosity decreases distinctly with increasing shear rate. More investigation also reveals that viscosity of gel increases with increasing concentration. Figure 10 shows that the shear stress needed to cause deformation also increases with increasing gel concentration.

CONCLUSION

The rheological behavior of UHMWPE gel was found to be affected by parameters of gel concentration, temperature, and shear flow using parallel plate rheometry. Summarizing the above results, we obtain the following findings. The gel point for concentration between 2 to 7% is between 101 to 108°C, and it increases with increasing gel concentration. Meanwhile, the G' of gel is found to be 1.5×10^3 Pa using strain sweep at 140°C. As strain increases, the G' exhibit a plateau and then reduces. A critical point at strain of 45% appears. The reason that G' reduces is because of extremely large deformation, which leads to destruction of the gel structure. The maximum G' is found to be at 140°C using strain sweep at various temperatures. According to the flow curves of gel at various temperatures, they all demonstrate the characteristics of a pseduoplastic fluid, and the curves at temperature higher than 120°C also behave likewise. The viscosity of gel increases distinctly with increasing gel concentration or decreasing temperature. As shear rate equals 1 s^{-1}, a critical point also appears, which alters the structure of gel. Such a critical point reveals the completion of formation of orientated structure, reduced flow resistance, and, consequently, reduced viscosity. According to rheological analysis, the optimum conditions for gel spinning will be at 6% UHMWPE gel and at 140°C.

Figure 9 The flow curves of shear rate and viscosity for UHMWPE gel at various concentrations and 160°C.

Figure 10 The flow curves of shear rate and shear stress for UHMWPE gel at various concentrations and 160°C.

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