

The Effect of Thermal Degradation on the Non-Newtonian Viscosity of an Aqueous Polyacrylamide Solution

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The objective of the present study was to investigate the effect of thermal degradation on the non-Newtonian viscosity of a dilute polymer solution by measuring the viscosity at a reference temperature before and after heating the solution with different heating temperatures and duration. The test solution was a polyacrylamide (Separan AP-273) 1,000 wppm solution in distilled water. The effect of thermal degradation on the viscosity was greater at relatively low shear rates than at intermediate and high shear rates. The viscosity of the polyacrylamide solution experienced at a relatively high temperature decreased more than that experienced at a relatively low temperature. In addition, the effect of thermal degradation on the viscosity of the polyacrylamide solution showed a strong dependence on the duration of heating.

Key Words : Thermal Degradation, Non-Newtonian Viscosity

Nomenclature

K : Fluid consistency index
 n' : Fluid behavior index
 T : Temperature
 t : time
 $\dot{\gamma}$: Shear rate (1/s)
 η : Viscosity

1. Introduction

Aqueous polymer solutions have been widely used for various industries such as polymer processing industry and HVAC industry. The wide uses of aqueous polymer solutions have been studied for heat transfer as well as flow characteristics. Shin and Cho (1994) investigated the effect of variable viscosity of an aqueous polymer solution on the heat transfer in a rectangular duct. Hartnett and Kostic (1985, 1989) reported that the heat transfer coefficients in the laminar flow through a rectangular duct with non-

Newtonian fluids (such as aqueous polyacrylamide (Separan AP-273) and Carbopol solutions) were approximately 300% greater than the values associated with constant-property fluids.

In the application of these fluids in electronic cooling, cooling liquids experience significantly higher temperatures than the room temperature. Note that the viscosity of the liquid is very sensitive to the temperature. For a non-Newtonian fluid, the viscosity depends not only on the temperature but also shear rate. Shin and Cho (1993) reported that for the polyacrylamide solution (1,000 wppm), the zero-shear-rate viscosity decreased significantly with temperature, whereas the apparent viscosity at intermediate and high shear rates varied much less. For a temperature-sensitive viscosity liquid, if the liquid recovers the original viscosity at the reference temperature after experiencing a high temperature, the liquid is often called thermally stable.

Knight (1973) and Shupe (1981) who studied the thermal stability of polyacrylamide solutions addressed the degradation problem in the long-term use of these solutions. Most methods to measure the thermal stability were time-consuming and expensive, and some were only applicable to solids. In the present study, we used the viscos-

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ity change of the polyacrylamide solution to monitor the stability of the solution. The measuring viscosity used to check the thermal stability of any non-Newtonian liquid has been reported in the literatures (Knight, 1973 and Shupe, 1981). However, most measurements did not show the viscosity versus shear rate data for non-Newtonian fluids. Hence, the objective of the present study was not only to report the viscosity data of a non-Newtonian fluid at different temperatures and heating durations but also to propose a method to monitor the thermal stability of an aqueous polymer solution at various shear rates using the steady shear viscosity measurement. Therefore, the steady shear viscosity of a polymer solution was measured over a range of shear rates and temperatures as well as heating durations at elevated temperatures.

2. Background

The degradation of polymer has been known for a long time, and there are several everyday examples such as the deterioration of cellulose in wood, rubber in car tires, the cracking and yellowing of paint films, etc. In general, the changes which occur in a polymer during degradation are manifested in a number of ways depending on the type of degradation process involved. Decreases in molecular weight, tensile strength, and change in the chemical structure can be listed as symptoms of degradation. Although they are no doubt connected each other, it is difficult to correlate these factors (Allen and Edge, 1989). Degradation depends on the environmental condition in which the polymer is used. For a polymer solution, violent mixing or pumping might result in the scission of long chains of polymer dissolved in a solvent, a phenomenon which is known as the mechanical shear degradation. Choi et al. (1992) studied the mechanical degradation effect of dilute polymer solutions on friction and heat transfer behavior in a closed loop system; they found that Polyox solution was very sensitive to mechanical shear degradation and degraded completely, thus losing its drag-reducing capability. On the other hand, polyacrylamide solution did

not degrade completely under a turbulent flow shear condition.

Thermal and thermo-oxidative degradations occur during processing or at elevated temperatures in an inert or oxidizing environment. The term polymer degradation is widely used in practice. Degradation always takes place in the presence of a specific amount of oxygen. Therefore, in hydrocarbon polymers, oxidation reactions are the most important means of structural breakdown (Allen and Padron, 1992). The dominant thermal and thermo-oxidative degradation mechanism may depend significantly on the structure and composition of the polymer. Since thermal degradation starts when a bond breaks, the strength of the weakest bond plays an important role in determining the thermal stability.

In addition, there are ultrasonic, hydrolytic, biological, photo, and chemical degradations. Photodegradation occurs when polymers are exposed to sunlight or high energy radiation. The polymer itself or impurities in the polymer absorb the radiation, inducing a reaction that leads to the loss of thermo-physical properties. In the case of high energy radiation polymer chains split directly (Allen and Padron, 1992). Some photodegradations are involved in photo-induced oxidation. Matthys (1985) reported the influence of photodegradation on the viscosity of antimisting polymer solutions (FM-9TM Imperial Chemical Industries) which showed an abrupt increase in their viscosity above a critical shear rate; photodegradation was found to increase the value of the critical shear rate and decrease the maximum post-gelation viscosity.

Degradation in polymers leads to a marked deviation from their original thermo-physical characteristics. In general, aqueous polymer solutions are not very stable compared with solid polymers. For example, guar gum is a seed galactomannan and is a shear-stable drag-reducing agent. However, the aqueous solution of guar gum is susceptible to microbio-degradation (Deshmukh and Singh, 1987), suggesting that the polymers may show different degradation characteristics with different solvents. Shupe who studied the stability of polyacrylamide (Pusher

TM-500, Dow Chem.) solutions reported the effect of metals, ferrous and ferric ion salts, pH, surfactants, antioxidants, oxygen and temperature on the chemical stability.

Bueche (1960) who studied the mechanism of the mechanical degradation of polymer solutions reported the effect of temperature and the presence of oxygen on degradation including the location of breaks in polymer chains. In general, thermal degradation requires breaking of chemical bonds. Once chemical bonds start to break, reactive terminating chains and other free radicals are created. Degradation can proceed either by depolymerization or by random chain scission (Van Krevelen, 1990 and Hergenrother, 1987).

Hu (1989) compared the viscosity data at a certain temperature before and after boiling: the higher the concentration of an aqueous solution, the more significant decrease in viscosity was observed at the low shear rate region. However, he did not consider the effect of heating duration on viscosity. An aqueous solution of Hydroxyethyl Cellulose (Natrosol-250 HHR, Hercules Inc.) showed much more significant thermal degradation than polyacrylamide (Separan AP-30, Dow Chemical) at the same concentration (i. e., 5, 000 wppm).

The thermal degradation would depend on both the temperature and the duration of heating. In the process of thermal degradation of a polymer at an elevated temperature, the thermal energy is accumulated, reaching the energy level that is high enough to break the chemical bonds in the polymer. Exposure to the elevated temperature in a relatively short period may not break the chemical bonds. However, an exposure to a relatively low temperature in a relatively long period may cause severe thermal degradation. An exposure to the temperature below a critical temperature in a long period may not result in any thermal degradation, relatively. Therefore, the effects of both temperature and the duration of heating on the thermal degradation should be considered.

3. Experimental Procedures

An aqueous solution of polyacrylamide (1,000

wppm Separan AP-273, Dow Chemical) prepared by dissolving the polyacrylamide powder in distilled water was chosen as a test fluid. The polyacrylamide solution was selected because it has been one of the most frequently used viscoelastic fluids in the literatures. It showed the significant laminar heat transfer enhancement in a rectangular duct [Shin and Cho, 1994, and Xie and Hartnett, 1992). Addition of very small amount of this polymer additive to a solvent liquid can significantly reduce the frictional pressure drop in a turbulent pipe flow. Hence, considerable studies have been conducted to understand this drag-reduction phenomenon because of its engineering potential, particularly when a large quantity of fluid has been transported over a long distance. However, polyacrylamide solutions degrade with decreasing viscosity as time goes. In order to improve the stability, stabilizers such as sodium thiocyanate, sodium nitrite, and methanol were recommended. Aqueous polyacrylamide solutions are known to be shear sensitive. At high shear rates, the molecular weight can be easily reduced due to the rupture of polymer chains (Othmer, 1982).

To make an aqueous solution of polyacrylamide (Separan AP-273), a required amount of the polyacrylamide powder for a given concentration was weighed using an electronic laboratory balance, and a required amount of water was also weighed. When about three-quarters of the water was poured in a beaker, the powder was sifted gently and slowly onto the water surface with a slowly rotating electromagnetic stirrer. In order to dissolve the powder stuck on the side wall of the beaker, the remaining one-quarter of the water was slowly poured in the beaker. With the electromagnetic stirring for a day, the agglomeration or lumping of the polymer could not be observed, and the solution was ready for testing.

The steady-shear viscosity of the polyacrylamide solution was measured as a function of shear rate by a falling needle viscometer and the Brookfield viscometer (model DV-I, Brookfield Co.). These instruments have been described in detail elsewhere (Shin and Cho, 1993). In order to keep a constant temperature during each vis-

cosity measurement, a thermal bath was used to circulate the temperature-controlled water into a water jacket surrounding the test cylinder of the falling needle viscometer or the Brookfield viscometer. For the present study, the uncertainty of the viscosity measurement was less than 2% with repeated measurements.

Viscosity measurements were conducted at the reference temperature of 20 before and after heating the test fluid. In order to see the effect of thermal degradation on viscosity, the fluid was gradually heated to a specific temperature (i. e., 40 or 60°C) over a period of 5 hours (8°/hr), and viscosity was measured at that temperature. Test fluids were allowed to maintain the temperature for next 24 hours. A small amount of test fluids were sampled periodically for viscosity measurement. Then the test fluid was cooled down slowly to 20°C and the viscosity was measured at 20°C using the Brookfield viscometer. The rate of temperature decrease was approximately 8–10°/hr.

4. Results and Discussion

Figure 1 shows the apparent viscosity vs. shear rate for a 1,000 wppm aqueous polyacrylamide (Separan AP-273) solution at three different temperatures, 20, 40, and 60°C. In general, the zero-shear-rate viscosity decreased significantly with temperature, whereas the apparent viscosity at intermediate and high shear rates (i. e., $\dot{\gamma} = 10$ –200 s^{-1}) varied much less. The results in Fig. 1 show the strong effect of temperature on the

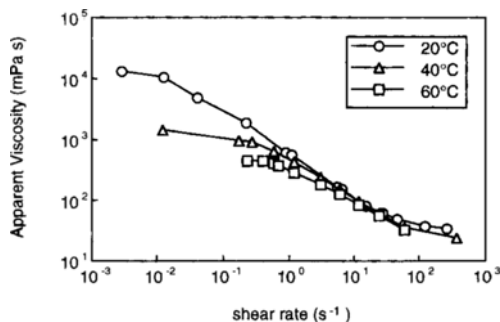


Fig. 1 Viscosity vs. shear rate curve for aqueous polyacrylamide solution (0.1%) at three different temperatures.

viscosity in the low shear rate region.

Figure 2 shows viscosities measured at the reference temperature of 20°C before and after heating. The test fluids were heated to and maintained at a relatively high temperature of 60°C for 8.0, 10.5, and 12.0 hours. As the heating period increased, the viscosities of the test fluids decreased more significantly at the low shear rate. It is evident that the viscosity decrease results from a thermal degradation of the aqueous polyacrylamide solution. However, it is not clear whether the viscosity decrease is caused by pure thermal degradation without thermo-oxidation. In order to exclude the thermo-oxidation, water used as the solvent for the solution should be replaced with another solvent such as formaldehyde or isobutane-alcohol.

Figure 3 shows viscosities measured at the reference temperature of 20°C before and after heating. The test fluids were heated to and maintained at 40°C for 9, 15, and 24 hours. When the test fluids were exposed to 40°C, a relatively low temperature, for 15 and 24 hours, the viscosity significantly decreased. The decrease in viscosities of test fluids at 40°C was smaller than that at 60°C, which indicates that the thermal energy needed to break polymer chains is strongly dependent on the exposure temperature. However, the viscosity of the test fluids heated for 24 hours at 40°C decreased to almost the same level as that obtained by test fluid heated for 12 hours at 60°C. This fact suggests that exposure to a relatively low temperature for a long period can cause the ther-

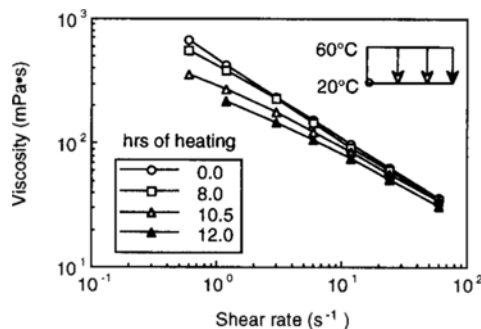


Fig. 2 Viscosity vs. temperature curve for aqueous polyacrylamide solution (0.1%) with four different heating durations at 60°C.

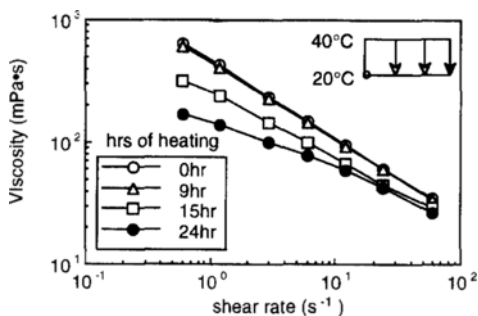
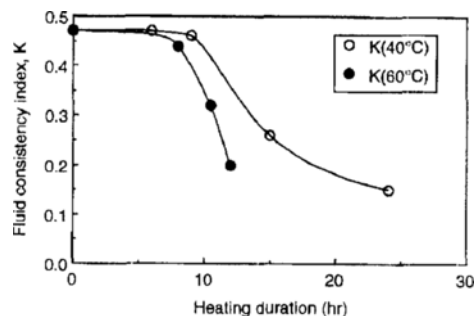


Fig. 3 Viscosity vs. temperature curve for aqueous polyacrylamide solution (0.1%) with four different heating durations at 40°C.

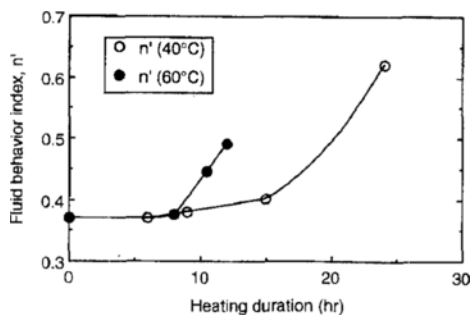
mal degradation as severe as a short exposure to a high temperature. Hence, thermal degradation should be examined as a function of both heating duration and exposure temperature.

Figure 4 shows the variation of fluid consistency index, K and fluid behavior index n' with heating durations. Both indexes of K and n' show a strong time-dependence. The index K decreases with increasing heating duration whereas the index n' increases with it. The slopes of K and n' -curves for a higher exposure temperature are steeper than that for a lower exposure temperature, respectively. It is worthy of note that both indexes of K and n' do not change with time for the initial period of heating duration. The fact implies that there is a critical time (Δt_c) required to accumulate the thermal activation energy to break chemical bonds in the polymer solution. When the test fluid is heated for more than the critical duration, the accumulated thermal energy is strong enough to break the polymer chains in an aqueous polymer solution. The critical duration is dependent on the exposure temperature. In Fig. 4, the critical duration for 60°C is slightly shorter than that for 40°C.

Since the viscosity vs. shear rate curves of polymer solutions have similar shapes at different temperatures, a method, known as the "method of reduced variables" has often been used to combine the viscosity data measured at different temperatures into one master curve. The method of reduced variables can be applied to the present viscosity data which are measured at various



(a)



(b)

Fig. 4 Variations of fluid indexes with heating durations.

heating durations with different heating temperatures. In order to get the master curve for viscosity, a two step procedure is used in the present study: (1) each curve obtained at a given exposure temperature was first shifted vertically upward by an amount $\ln(K_0/K)$, and (2) the resulting curve was then shifted horizontally to superpose on the reference curve obtained at a reference temperature with zero heating duration.

Figure 5 shows the master curves for both the fluid consistency index, K and the fluid behavior index, n' . Both of the indexes show "Arrhenius dependence" of the form, which is commonly used in the temperature dependence of the shift factor, a_T as Bird et al. (1987) explained. The present study propose the following correlations of K and n' with heating duration and exposure temperature:

$$K = K_0 \exp \left[- \left(\frac{t - t_c}{C_1} \right) \left(\frac{1}{T_{ref}} - \frac{1}{T} \right) \right] \quad (1)$$

$$n' = n'_0 \exp \left[\left(\frac{t - t_c}{C_2} \right) \left(\frac{1}{T_{ref}} - \frac{1}{T} \right) \right] \quad (2)$$

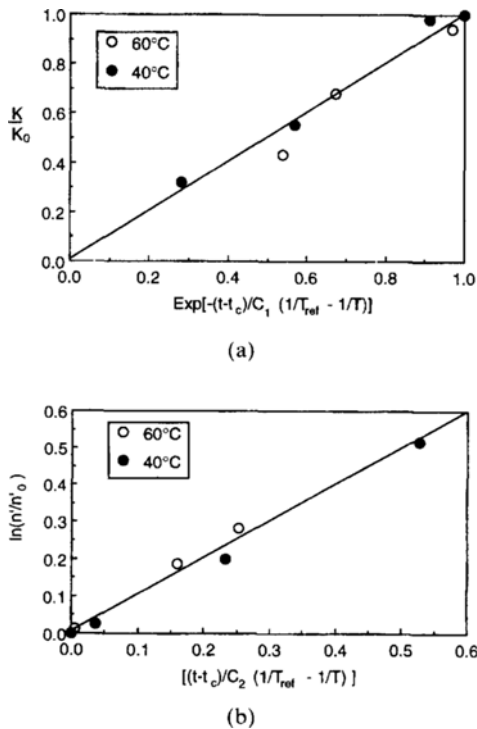


Fig. 5 Master curves for both indexes of K and n' .

Here, T is in K and t is the heating duration in second. The constants C_1 and C_2 are 10 and 24, respectively. The reference temperature (T_{ref}) is 20°C (293K). Here, $\Delta t (= t - t_c)$ represents the accumulation time for degradation. The critical duration used in the present study is 7.9 hours for both temperatures.

5. Conclusions

In an attempt to develop the advanced non-Newtonian energy transmission fluids that would enhance heat transfer and yield friction reduction in a non-circular duct, thermal stability tests measuring steady-shear viscosity have been conducted with an aqueous 1,000 wppm polyacrylamide solution. The viscosity was measured at the reference temperature, 20°C, with test fluids heated to either 40 or 60°C for different heating periods. In the present study, the aqueous polyacrylamide solution showed the significant decrease in viscosity with heating duration, particularly at low shear rates, the phenomenon which

is related to the degradation of the polymer. Furthermore, thermal degradation of the aqueous polymer solution was strongly dependent on temperature which the test fluids were exposed to. Exposure to a high temperature caused severer degradation than to a low temperature.

The present study proposes the new correlations for the fluid consistency index, K and the fluid behavior index, n' . The proposed correlations can be used for the modeling of thermal degradation in numerical analyses. Also, the present study proposes a checking method of thermal stability for polymer solutions by viscosity measurements in relatively low shear rate region.

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