Mechanical degradation kinetics of poly(ethylene oxide) in a turbulent flow

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Abstract

Turbulent drag reduction (DR) efficiency of water soluble poly(ethylene oxide) (PEO) with two different molecular weights was studied as a function of polymer concentration and temperature in a turbulent flow produced via a rotating disk system. Its mechanical degradation behavior as a function of time in a turbulent flow was also analyzed using both a simple exponential decay function and a fractional exponential decay equation. The fractional exponential decay equation was found to fit the experimental data better than the simple exponential decay function. Its thermal degradation further exhibited that the susceptibility of PEO to degradation increases dramatically with increasing temperature.

Keywords : Turbulent drag reduction, mechanical degradation, poly(ethylene oxide), decay function

1. Introduction

A large amount of energy loss due to friction occurs in many cases of turbulent flow, generally. However, it is well known that turbulent drag reduction (DR) which is a drastic reduction of frictional resistance can be easily observed by injecting a minute amount of polymeric additives in a turbulent flow (Kulicke and Kötter, 1989). Polymer solutions undergoing a turbulent flow in a pipe thereby require a lower pressure drop to maintain the same volumetric flow rate. The addition of small amounts of additives to the flowing fluids can show significant effects on a lot of flow types, including the stability of laminar flow, transition to turbulence, vortex formation and break-up (Sreenivasan and White, 2000).

Effective polymeric DR additives are considered to be flexible, linear with a high molecular weight (Choi and Jhon, 1996) such as poly(ethylene oxide) (PEO) (Kim et al., 1999), poly(acrylamide) (PAAM) and polyisobutylene (PIB). The dependence of DR efficiency is known to be a function of polymer molecular weight, polymer concentration, and the degree of turbulence. Injecting only 10 – 50 ppm stock solution of a polymer additive in a tube can often produce a drag reduction more than 50%, implying that the energy cost necessary to transport the fluid is reduced by the same amount. However, the usage of these polymers is limited because of their susceptibility to flow-induced shear degradation (Choi et al., 2000). Recently,

Choi et al. (2002) reported that the double-stranded lambda DNA is a better drag reducer when compared with the linear polymers. They also found that the drag reducing capability disappeared when the DNA denatures to form two single-strand molecules, and the DNA is always cut in half in turbulent flow. Cationic surfactant systems (Sung et al., 2003) as high resistant materials to turbulent flow have been also investigated.

This DR phenomenon has been the subject of its scientific concern (Jhon et al., 1987; Amarouchene and Kellay, 2002; Choi and Jhon, 1996) and experimental research (Kulicke et al., 1989; Yoon et al., 2002). The industrial applications of DR can be found in many areas such as transport of crude oil (Burger et al., 1980), closed-circuit pumping installations such as central-heating systems (Sellin et al., 1982), sewage systems to prevent overflowing after heavy rain (Sellin and Ollis, 1980), hydraulic transportation of solid particle suspensions (Golda, 1986), fire-fighting to increase the range of water jets, and water supply and irrigation systems (Sellin et al., 1982).

Although the DR was discovered almost half a century ago, the physical mechanisms responsible for the phenomenon of drag reduction are not completely understood and remain a subject of debate (Balkovsky et al., 2000; Chertkov, 2000; Groisman et al., 2001; Odijk, 2001; de Gennes, 1986). Nevertheless, it is generally accepted that both the viscoelastic property including elastic behavior and energy dissipation phenomena of polymer solutions and the interaction between polymer molecules and turbulence generate the DR phenomenon. The role of stress anisotropy due to polymer extension versus elasticity is

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also still an ongoing subject of controversy in the DR mechanism. In addition, the additives demonstrate a desirably high DR efficiency while so undesirable mechanical degradation under turbulent flow occurs. Therefore, molecular degradation is one of the major defects in the DR application, since the polymeric additives are exposed to strong turbulent elongational strain and shear stresses. The mechanical degradation process was assumed to be that the polymer chains can indeed be fully extended by turbulent flow and experience the chain midpoint scission of macromolecule (Horn and Merrill, 1984). The mechanical degradation of high molecular weight polymers such as PEO and PIB under turbulent flow was investigated by various conditions of temperature, polymer concentration, and rotation speed. Since the long chain polymer experiences mid-point degradation, the polymer chains having different molecular weights will show different time dependent resistance. In other words, longer molecules are more susceptible to mechanical degradation, accompanying more rapid degradation (Rho *et al.*, 1996).

In this study, the DR efficiency which has been investigated by dilute aqueous solutions of PEO with two molecular weights in a rotating disk system (RDS) in our previous work is reanalyzed focusing mainly on their mechanical degradation kinetics (Yang *et al.*, 1991). The empirical and fractional exponential decay functions of PEO were adopted to examine their time-dependent drag reduction efficiency. Relations between the decrease in drag reduction with shearing time and the thermal effect on polymer degradation were also studied.

2. Experimental

The water-soluble PEO series, with two different weight average molecular weights of 4.0×10^6 and 5.0×10^6 g/mol, were acquired from Scientific Polymer Products Inc. Its aqueous stock solutions were initially prepared with 0.5 wt% concentration using deionized water and allowed to be stabilized for 4 or 5 days. The stock solutions were diluted to a desirable concentration with mild stirring to avoid any polymer degradation during sample preparation. Dilute polymer solutions for the DR experimentation were prepared by carefully injecting the measured quantities of stock solution directly into the turbulent flow. Concurrently, 1 wt% isopropanol was also added into the stock solution to prevent chemical degradation of the polymer used.

A RDS which is the same as previously described (Choi and Jhon, 1996) is used to study both the DR efficiency and the transient behavior of mechanical degradation of PEO in a turbulent flow. The RDS consists of a stainless steel disk with a dimension of 10.1 cm in diameter and 0.32 cm in thickness, and is enclosed in a thermostatically controlled cylindrical container made of stainless steel with dimensions of 16.3 cm in diameter and 5.5 cm in height.

A volume of polymer solution required to fill the container was approximately $1.1l$. A DC motor generator coupled with a controller (Cole Parmer Master Servodyne Unit, USA) was used to maintain a preset rotational speed by measuring a variable torque as required by the load on the disk. All experiments were performed at $25 \pm 0.5°C$, unless specified otherwise. The fluid temperature and the rotational speed were measured by a K-type thermocouple and a digital tachometer, respectively. •

The rotational Reynolds number (N_{Re}) can be described in an RDS system as $N_{Re} = \rho r 2\omega/\mu$. Here, ρ and μ are the fluid density and fluid viscosity, r is a disk radius, and ω is the disk rotational speed. All experiments were performed at the rotational speed of 2,800 rotations per minute (rpm) corresponding to water-based N_{Re} of 8.3×10^5. The turbulence is well known to be generated for $N_{Re} > 3 \times 10^5$ or equivalently 1,050 rpm using this RDS (Choi and Jhon, 1996).

DR characteristics were examined by measuring the torque of distilled water at a given speed. The percent drag reduction is then determined by measuring the corresponding torque required in a dilute polymer solution at the same speed using the following Eq. (1) (Kim *et al.*, 2000),

$$DR(\%) = \frac{T_o - T_p}{T_o} \times 100. \tag{1}$$

Here, T_o is the torque measured in distilled water, and T_p is the torque measured in polymer solution.

Furthermore, steady shear viscosity of the PEO stock solution (0.5 wt%) was measured using a rotational rheometer (Physica, MCR-300, Germany) with a Couette cell geometry (DG 26.7) at various temperature (at 25, 40, and 60°C) (Tirtaatmadja *et al.*, 2002).

3. Results and discussion

Fig. 1 represents the dependence of DR efficiency on polymer concentration for two different molecular weights of PEO. The DR efficiency of higher molecular weight is larger than that of lower molecular weight in a whole polymer concentration range up to 250 wppm at the RDS rotational velocity of 2800 rpm. The concentrations showing the maximum drag reduction at different molecular weight called optimum concentrations have been found to be related with the combination of the two following factors: the drag-reducing property of the solute polymer and the increasing viscosity of the solutions, which becomes increasingly significant at higher concentrations of the polymer (Choi and Jhon, 1996). Since the polymer-induced turbulent drag reduction is induced by the viscoelastic behavior contributions from the individual polymer molecules, the increment of polymer concentration increases the drag reduction efficiency. Furthermore, note that since the total drags of pipe flow (inner flow) and rotating disk flow (outer flow) are different, a maximum of 80 % of the
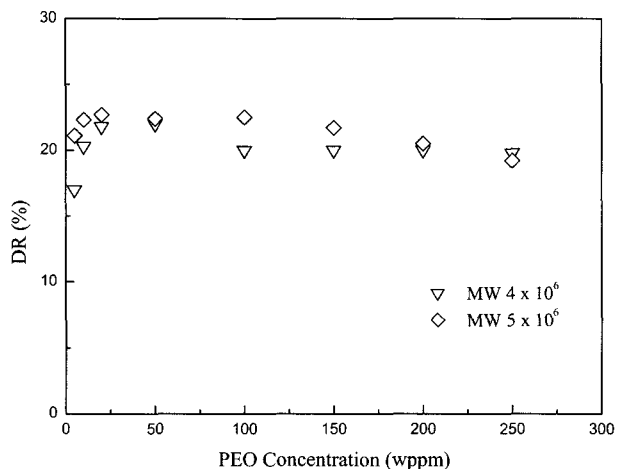
Fig. 1. Drag reduction efficiency *vs.* PEO concentrations of two molecular weights.

DR can be achieved in a pipe flow, while only 40% of the maximum DR efficiency can be obtained for rotating disk flow (Choi *et al.*, 1996).

Figs. 2(a) and 3(a) show the DR efficiency profiles of PEO (Mw = 4 × 10⁶ g/mol) and PEO (Mw = 5 × 10⁶ g/mol), respectively for three different concentrations of 50, 150 and 250 wppm. The DR behavior in turbulent flow is appeared to be related with elongational straining as well as shearing force, in which these cause the breakage of main chain of the polymer by the mechanical energy.

The degree of mechanical degradation has been reported to be higher in poor solvents than those in good solvents (Kakano and Minoura, 1975). As the mechanical degradation is associated with bond breaking due to chain stretching by the flow, it is still not clear how the conformation change affects this breaking mechanism (Lim *et al.*, 2003). The adoptability of λ-DNA supports the validity of simple degradation model in fitting the degradation curve of λ-DNA applying a Brostow model (Brostow *et al.* (1990)), in which the points on the chain where changes of direction occur are more vulnerable to chain scission. Depending on their specific location, some of them might be protected from degradation by their surroundings, while others will undergo scission during flow. The average numbers of points per chain are proportional to the number of the breakable sequences having two different orientations and changing, and also can be related to drag reducer concentration.

The following single-relaxation decay model was adopted to explain a time-dependent relative DR efficiency which is related to the mechanical degradation (Bello and Müller, 1996; Lee *et al.*, 2002) as given in Eq. (2). The empirical equation associates with a slow relaxation time of the polymer solution.

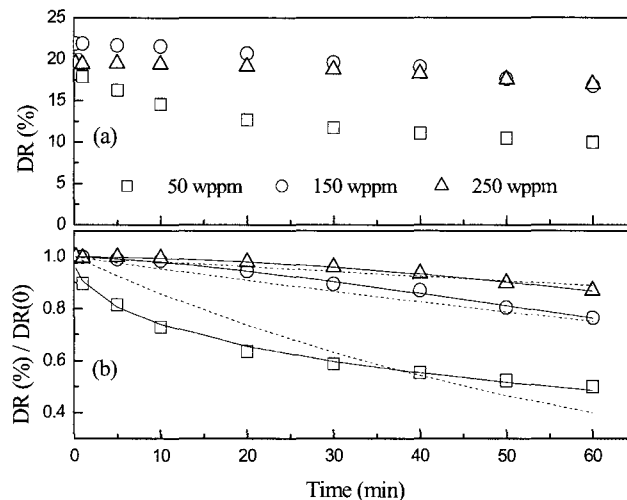$$DR(t)/DR(0) = \exp(-t/\lambda_s) \qquad (2)$$

Fig. 2. (a) Drag reduction efficiency as a function of various concentrations of PEO (Mw = 4 × 10⁶ g/mol) and (b) $DR(t)/DR(0)$ *vs.* time of the shear degradation of PEO (Mw = 4 × 10⁶ g/mol). Dotted lines are obtained from Eq. (2), solid lines are obtained from Eq. (3), and symbols are the experimental data.
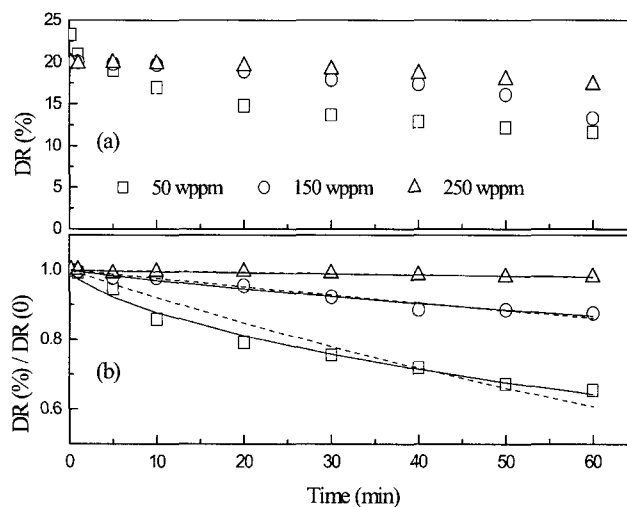

Fig. 3. (a) Drag reduction efficiency as a function of various concentrations of PEO (Mw = 5 × 10⁶ g/mol) and (b) $DR(t)/DR(0)$ *vs.* time of the shear degradation of PEO (Mw = 5 × 10⁶ g/mol). Dotted lines are obtained from Eq. (2), solid lines are obtained from Eq. (3), and symbols are the experimental data.

Here $DR(t)$ and $DR(0)$ are the percent drag reduction efficiency at times t and $t = 0$, respectively. The $1/\lambda_s$ quantifies the loss rate of drag-reduction activity or the rate of degradation. Despite the successful applicability of this single exponential decay model for shear resistant drag reducers especially in describing short time degradation behavior, it is not difficult to conjecture the inadequacy of this model. As shown in Figs. 2(b) and 3(b) with dotted lines, it is

found that Eq. (2) does not fit the experimental data relatively well. Therefore, to improve the fitting, a fractional exponential form, often called the Kohlrausch, Williams, and Watt (KWW) function, which has been modified from the single exponential decay function shown in Eq. (3) is introduced. This equation has been used to describe the second order nonlinear relaxation behavior.

$$DR(t)/DR(0) = \exp[-(t/\lambda_F)^{1-n}] \tag{3}$$

Here, λ_F is an observed time scale of the relaxation process and n is a fractional exponent i.e. the degree of non-exponetiality considering the breadth of the distribution of relaxation time. The KWW function has been applied in various areas of entangled polymer melt dielectric relaxation processes (Rendell and Ngai, 1984). Figs. 2(b) and 3 (b) with solid lines show that the relative drag reduction effectiveness was fitted better with Eq. (3) than Eq. (2). The λ_s s obtained using Eq. (2) for the various PEO (Mw = 4×10^6 g/mol) concentrations in Fig. 2(b) are estimated as 65.3 min for 50 wppm, 209.6 min for 150 wppm, and 510.7 min for 250 wppm. Note that $1/\lambda_s$ decreases with increasing the polymer concentration. The higher concentration of PEO shows a more enhanced relative drag reduction effectiveness. The λ_F for the various PEO concentrations from Eq. (3) are 116.8 min for 50 wppm, 150.6 min for 150 wppm, and 180.1 min for 250 wppm, respectively.

Furthermore, the λ_s obtained from Eq. (2) for various PEO (Mw = 5×10^6 g/mol) concentrations are estimated as 120.5 min for 50 wppm, 402.1 min for 150 wppm, and 2671.6 min for 250 wppm. On the other hand, the λ_F for the various PEO concentrations in Fig. 3 (b), obtained from Eq. (3), are 200 min for 50 wppm, 598.9 min for 150 wppm, and 10421 min for 250 wppm, respectively.

Fig. 4 illustrates the decreases in both the drag reduction efficiency and the viscosity-average molecular weight as a function of time for different molecular weights of PEO. The viscosity-average molecular weight was calculated from the intrinsic viscosity measurement of the polymer solution via the Mark-Houwink relationship as following :

$$[\eta] \equiv \lim_{c \to 0} \eta_{sp}/c = 1.25 \times 10^{-4} \overline{M_v}^{0.78} \quad \text{(at 30°C)} \tag{4}$$

It clearly indicates that the higher molecular weight PEO (Mw = 5.0×10^6 g/mol) degrades more rapidly over the entire shearing time than that of lower molecular weight, since the larger molecules are subjected to experience the higher breaking force at the same rotational speed. The DR efficiency is largely dependent on the contributions of the molecular weight distribution in the higher molecular weight species.

Fig. 5 shows the effect of temperature on thermal degradation of relative drag reduction, $DR(t)/DR(0)$, examined with 50 wppm PEO at three different temperatures (25°C,
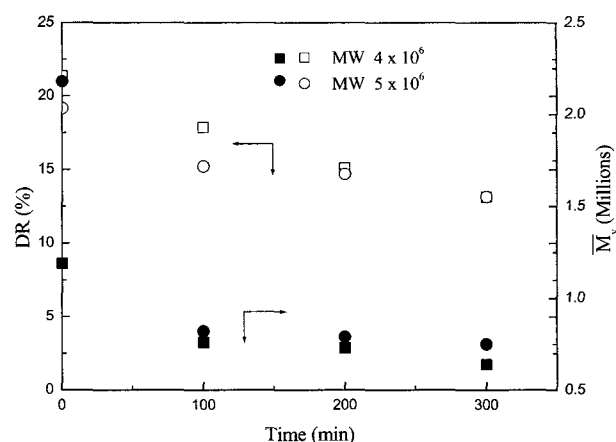

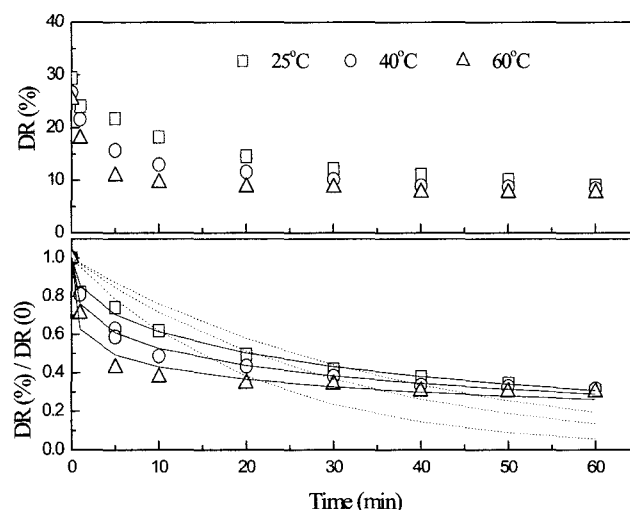Fig. 4. Drag reduction efficiency and viscosity-average molecular weight vs. time of 300 wppm.

Fig. 5. $DR(t)/DR(0)$ vs. time to study the shear degradation of 50 wppm PEO (Mw = 5×10^6 g/mol) at three different temperatures (25°C, 40°C, and 60°C). Dotted lines are obtained from Eq. (2), solid lines are obtained from Eq. (3), and symbols are the experimental data.

40°C, and 60°C). The initial DR efficiency value was 29.39 % at 25°C, 26.7% at 40°C, and 25.3% at 60°C, respectively. The λ_s obtained from Eq. (2) for the various temperatures are estimated as is 36.60 min at 25°C, 29.96 min at 40°C, and 20.74 min at 60°C, respectively. The λ_F for the various temperatures in Fig. 5, obtained from Eq. (3), are 42.83 min at 25°C, 33.52 min at 40°C, and 19.37 min at 60°C, respectively. As we increased the temperature and fixed the rotational speed of the disk to be 2,800 rpm, the N_{Re} also increased due to the decrease of the solution viscosity. Fig. 6 represents the shear viscosity of the polymer solution as a function of applied shear rate. Shear viscosities of the PEO solution at three different temperatures of 25, 40, and 60°C were obtained to be 1.03, 0.84, and 0.78 cP, respectively. Furthermore, it can be also notes that PEO exhibits
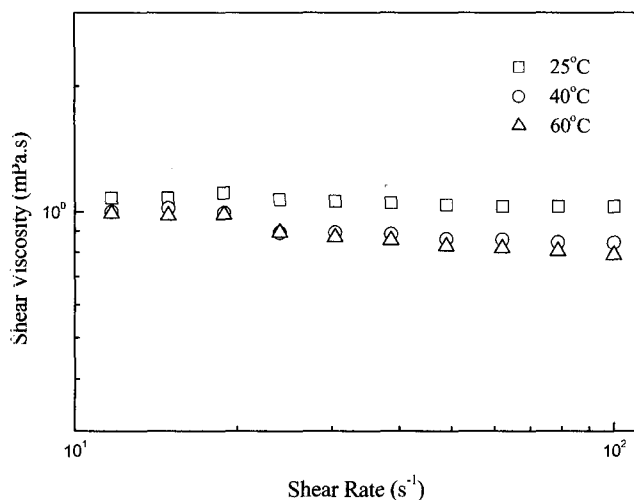
Fig. 6. Shear viscosity *vs.* shear rate of PEO (Mw = 5 × 10⁶ g/mol) stock solution with 0.5 wt% at three different temperatures (25°C, 40°C, and 60°C).

а lower critical solution temperature with a theta temperature at 96°C in pure water (Ataman and Boucher, 1982), indicating that a size of the polymer chain (PEO) decreases as the system approaches to a theta temperature with a temperature increase.

4. Conclusions

Turbulent drag reduction with PEO in an RDA was investigated with two different molecular weights. A higher molecular weight of PEO (Mw = 5.0×10^6 g/mol) showed less mechanical degradation than that of with a lower molecular weight (Mw = 4.0×10^6 g/mol) at the same concentration. Its mechanical degradation behavior in a turbulent flow was examined by using both an empirical exponential decay function and a fractional exponential decay equation. The KWW decay function fits experimental data better than the empirical exponential decay function. It was also found that susceptibility of the PEO to degradation increases dramatically with increasing temperature.

Acknowledgement

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