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ORIGINAL ARTICLE

The effect of polymer concentration and temperature on the rheological behavior of metallocene linear low density polyethylene (mLLDPE) solutions

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Abstract In this study, the rheological characteristics of metallocene linear low density polyethylene (mLLDPE) were analyzed. Cyclohexane was used to prepare the dilute solutions of mLLDPE. The concentrations used in this study ranged from 1000 to 4500 ppm with 1000 ppm increments. The test temperatures ranged between 293 and 323 K at 10 K increments. The shear rate range was from 0.8 and 600 s^{-1}. Rheological measurements were performed on a rotational rheometer model AR-G2 with parallel plate geometry. The solution rheology was affected by shear rate, polymer concentration, and testing temperature. Different models were used to describe the rheological behavior of the mLLDPE dilute solutions. A model that accounted for concentration was successful in describing the rheological behavior as compared to models that were developed for polymer melt, which do not take the polymer concentration into account.

1. Introduction

The knowledge of solution or melt rheology of polymers is keystone information for the polymer processing industry. Understanding the solution rheology of polymers is a key factor in developing suitable models for the solution polymerization process. AL-Fariss and Al-Zahrani (1993), Osswald (1998), Mills (2005), and Birley et al. (1992) showed that rheological behavior of polymers is of utmost importance regarding different polymer processing methods such as extrusion, injection molding, blow molding, calendaring, and fiber spinning. Polymer solutions have distinct industrial applications. For example, polymethyl methacrylate (PMMA) is added in about 2% to motor oil to reduce the dependency of

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the oil on the temperature. More concentrated solutions, 40% polymer or more, are used to manufacture textile fibers by the process of solution spinning. Paints and coatings are other industrial applications of polymer solutions.

From ‘‘*definition*’’ point of view, it is not easy to distinguish between ’’*dilute*’’ and ’’*concentrated*’’ polymer solutions. Usually there is a gradual transition from the behavior of dilute to that of concentrated solutions. As a rule of thumb, a polymer solution may be called concentrated if the solute concentration exceeds 5% by weight. Formulas describing the viscosity behavior of dilute polymer solutions were presented by Van Krevelen (1990) and others. For concentrated polymer solutions, there are other correlations given by Van Krevelen and others as well (1990).

The viscosity of the polymer solution depends on a number of factors. Van Krevelen (1990) mentioned that some of these factors include molecules' shape, molecular weight, hydrophilic nature, and interaction of polymer molecules with the solvents. Additionally, the solution viscosity depends on the concentration of the dissolved polymer. In good solvents the polymer segments prefer to be surrounded by solvent molecules rather than by other polymer segments. On the other hand, in poor solvents, the polymer molecules try to minimize the area of contact with the solvents molecules, i.e., the extension of the polymer molecule depends on the interaction of the polymer solvent, which directly affects its size and the viscosity of the solution as explained by Al-Zahrani (1990). Most polymers melt and solutions are non-Newtonian, meaning that their viscosity depends on factors other than the velocity gradient. Except for rare cases, the viscosity of polymer melts and solutions decrease as the shear rate increases. This could be explained by the alignment of the polymer molecules under the application of the shear. This molecular alignment will allow easier flow of the molecules, which reduces the viscosity at higher shear rates. This is called shear thinning. This phenomenon is described by the famous power law formulated by Ostwald and Waels shown in Eq. (1):

$$\tau = k \cdot \gamma^{n} \tag{1}$$

$$\eta = k\gamma^{(n-1)} \tag{2}$$

where τ is the shear stress, γ is the shear rate, k is constant and n is the power low parameter. The temperature of the polymer solution, T, has a profound effect on its viscosity, η. The dependence of viscosity η on temperature T could be described by Arrhenius equation as depicted in Eq. (3).

$$\eta = k_1 \exp(E_0/RT) \tag{3}$$

where, k_1 is constant, R is gas constant and E_0 is activation of energy.

In this study, the rheological models used for investigating of flow behavior of the polymer were Cross model, Eq. (4), Carreau model, Eq. (5), Power law model, Eq. (1), and Alfariss et all model, Eq. (6), to study the shear stress and shear rate relationships.

$$\frac{\eta - b}{a - b} = \frac{1}{(1 + ((c \cdot \gamma)^{d})} \tag{4}$$

$$\frac{\eta - b}{a - b} = \frac{1}{(1 + (c \cdot \gamma^{2}))^{\frac{d}{2}}} \tag{5}$$

Table 1 summarizes some of the models that are used to describe the polymer viscosity as a function of shear rate and temperature as were cited by Amin et al (1980). Whereas, Table 2 lists models that relate the polymer solution viscosity to concentration, shear rate, and temperature as explained by AL-Fariss and Al-Zahrani (1993) and Al-Zahrani (1990).

AL-Fariss and Al-Zahrani (1993) and Al-Zahrani (1990) studied the rheological behavior of some dilute aqueous polymer solutions. They related the measured viscosity to shear rate, temperature, and concentration using the following equation.

$$\eta = A_1[\exp^{(B_1/T)}]\gamma^{C_1}\exp^{(D_1 * C)} \tag{6}$$

where η is viscosity of polymer solution, γ is shear rate, T is temperature, C is polymer concentration and A_1, B_1, C_1, and D_1 are constants. They proposed this correlation to predict the viscosity of polymer solution as a function of temperatures, shear rates and concentrations.

The rheological properties of polyethylene solutions did not get enough attention in the literature. Yasuo et al. (1994) studied the rheological behavior of very dilute solutions of ultra high molecular weight polyethylene (UHMWPE) for its utilization in the gel spinning technology. Their investigation was mainly focused on the shear flow viscosity of these solutions. They found that, such polyethylene solutions exhibit a shear thinning behavior at a very wide range of shear rate from 10^{-4} to 10^{3} s^{-1}. Furthermore, this typical non-Newtonian behavior was more obvious by increasing the PE concentration in their solutions.

Table 1 Correlations for viscosity prediction of liquids as a function of temperature.

Date	Investigator	Relationship
1913	de Guzman	$d\ln\phi/dT = W/\mathrm{RT}^2$
1916	Arrhenius	$d\ln\eta\upsilon^{1/3}/dT = k/T^2$
1923	Raman	$\eta_1 = \eta_v\, e^{(E2 - E1)/\mathrm{RT}}$
1925	Fulcher	$\ln\eta = A + B/(T + C)$
1926	Dunn	$\eta = Ae^{Q/\mathrm{RT}}$
1926	Frenke	$\eta = XTe^{U/\mathrm{RT}}$
1930	Madge	$\eta = Ae^{BT}/(T - C)$
1930	Andrade	$\eta v^{1/3} = Ae^{B/\mathrm{Tv}}$
1933	Silverman	$\eta = (A/T^{0.5})e^{(B/T - \mathrm{ct})}$
1936	Eyring	$\eta = (N\,h/V)\, e^{\Delta E/\mathrm{RT}}$
	Modified forms of Eyring Equation	$\eta = (A/V)e^{\mathrm{BT}}b^{/T}$
1952	Litovitz	$\ln\eta = A + a/\mathrm{RT}^3$
1955	Gornlissen and Waterman	$\eta = e^{B + A/\mathrm{Tc}}$
1955	Girifalco	$\ln\eta = C + (B/T) + (A/T^2)$
1971	Agrawal and Thodes	$\eta + k = ae^{m/\mathrm{Tr}}$
1972	Valzen	$\ln\eta = B[(1/T)-(1/T_0)]$

Table 2 Correlations for viscosity prediction of liquids as a function of temperature and concentration.

Date	Investigator	Relationship
1993	Al-Fariss and Al-Zahrani (1993)	$\eta = A_1[\exp^{(B_1/T)}]\gamma^{C_1}[\exp^{(D_1 * C)}]$
1998	Al-Fariss and Al-Zahrani (1998)	$\eta = \frac{B_1}{\gamma}[(\frac{\gamma + A_1}{A_1})^n - 1]^{(1/n)} * \exp^{(C_1/T + D_1 * C)}$