Rheological behavior of polymer melt in the electric field

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Abstract. The electric field is applied to polymer processing, a theoretical framework is established for understanding the physical characters of the procedure. The theoretical analysis shows that electric field can result in decreasing the elasticity, the entanglement density and the viscosity of polymer melts.

1. Introduction

The electrostatic force has been widely used in the electrospinning process [1-4], where a high voltage is used to create an electrically charged jet of polymer solution or melt, which dries or solidifies to leave a polymer fiber. From many experimental phenomena and theoretical analysis, the fiber diameter decreases with increasing electric potential [5-8].

In traditional extrusion methods such as various types of screw extruder, the material being processed has a high viscosity and elasticity, so there are limits to increasing output and improving the quality of the extrusion. Recently, the electric field has been introduced into polymer processing [9], which can lower the viscosity and the elasticity of the melt, so the flow resistance can be lowered correspondingly. In the electric field, the chain of the electriferous polymer melt can be drawn and be orientated. Therefore, it can be induced that the entanglement density decreases and the number of vacant sites increases. In a result, it is in favor of the reptation of molecular quickly, which means the viscosity decreased. Moreover, it can be made the molecular chain in better order, which can improve the performance of the processing product.

But until now, there has no any theoretical framework for understanding the physical mechanisms of polymer melts in the electric field. In this paper, we will develop a mathematic model to describe the effect of the electric field on the molecular chain orientation, and explain the change of the viscosity and the elasticity of the polymer melt.

2. Elasticity and Viscosity

Figure 1 describes the velocity of polymer melts in the extrusion. Where \( L \) is the length of the extrusion head, \( R \) is the radius of the extrusion head, \( \Delta P \) is the pressure difference between the entrance and the exit of the extrusion head. The following assumptions will be made:

1. The melt flow is laminar in axial \( z \)-direction, and isothermal;
2. The melt is uncompressible and viscoelastic, the density \( \rho \) is unchangeable;
3. Gravitational effects may be neglected.

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When imposed the electric field, the shear stress includes two parts, one is the tangential stress caused by the electric field $\sigma E$, where $\sigma$ is the surface charge density; the other is the viscous stress $\tau_\pi = \frac{\Delta P \cdot r}{2L}$ [10–11]. So the total shear stress is:

$$\tau = \left(\frac{\Delta P \cdot r}{2L} + \sigma E\right)$$ (1)

For conveniently, we select the power constitutive equation:

$$\tau = -K \cdot \dot{\gamma}$$ (2)

Where $K$ is the viscosity, $n$ is the non-Newtown index, so the shear rate is:

$$\dot{\gamma} = \left(\frac{\tau}{K}\right)^{\frac{1}{n}} = \left(\frac{\Delta P \cdot r}{2KL} + \frac{\sigma E}{K}\right)^{\frac{1}{n}}$$ (3)

The surface charge density is:

$$\sigma = \frac{U \varepsilon \varepsilon_0}{L_0}$$ (4)

where $U$ is the voltage drop between the capacitor plates, $\varepsilon$ is the dielectric constant, $\varepsilon_0$ is the vacuum dielectric constant, and $L_0 \approx L$ is the distance between the capacitor plates.

It is also easy to know that the electric field can be expressed as:

$$E = \frac{U}{L_0}$$ (5)

The polarized intension $p$ and the distortion $S$ can be described as following:

$$p = d\tau_e + aE$$ (6)
where $d$ is the piezoelectricity coefficient, $\tau_e$ is the stress caused by the electric field, $J_0$ is the elastic module when $E = 0$, and $\alpha$ is a stress constant when $\tau_e = 0$.

From equation (6) and equation (7), there are:

$$\tau_e = \frac{p - aE}{d}$$

$$S = J_0 \frac{p - aE}{d} + dE$$

Therefore,

$$\tau_e = GS = GJ_0 \frac{p - aE}{d} + dGE$$

Comparing between equation (8) and equation (10), there is:

$$(1 - GJ_0) \frac{p - aE}{d} = dGE$$

where the elastic module is $G = G_0 + \Delta G$, and $G_0$ is the elastic module in the equilibrium state, and $\Delta G$ is the increment.

Equation (11) can be expressed in the form:

$$- \Delta GJ_0 \frac{p - aE}{d} = dGE$$

Obviously, $\Delta G < 0$, that means the elasticity decreases with the elastic module decreasing in the electric field.

Figure 2. The relationship between the viscosity and the voltage.
The viscosity in the wall is:

\[
\eta_w = \left. \frac{\tau}{\gamma} \right|_{r=R}^{\frac{K \cdot \gamma}{r=R}} = K \cdot \frac{n}{\gamma} = K \cdot \left( \frac{\Delta P \cdot R}{2KL} + \frac{\sigma E}{K} \right) \left( n^{-1} \right) ^{n}}^{(13)}
\]

So there is:

\[
\eta_w = K \cdot \left( \frac{\Delta P \cdot R}{2KL} + \frac{U^2 \varepsilon_0}{KL^2} \right) \left( n^{-1} \right) ^{n}}^{(14)}
\]

From equation (14), the relationship between the viscosity and the voltage can be obtained. Figure 2 describes their relationship for LDPE, the temperature of the melt is 150 degrees centigrade, and \( \varepsilon_0 = 8.85 \times 10^{-12}, K = 14700, n = 0.35, \varepsilon = 2.3 \). From this figure, the viscosity decreases with the voltage increasing obviously.

3. Entanglement Density

Polymer melts are often assumed to have an entangled network structure. The flow behavior of polymer melts seems to be dominated by the entanglement phenomenon. Although the detailed nature of the entanglement is not entirely understood, it is a common assumption to consider the polymer molecules in a melt to be organized in a network of the entanglements that are temporary junctions. These entanglements can slide along the chains, disappear and reform continuously and they can translate, rotate and deform with the liquid changing. When imposing the electric field, the chain of the electriferous polymer melt can be drawn and be orientated, such as in figure 3.

![Figure 3. Orientated chains of polymer melt in the electric field.](image)

Using the same method like in Ref. [11–12], the kinetic rate equation for polymer melts in electric field can be described as following:

\[
\frac{dx}{dt} = \frac{k_1}{\lambda} (1 - x)
\]
\[
\frac{dx}{dt} = k_2 \left( \frac{\Delta P \cdot r}{2KL} + \sigma E \right)^{1/n} x
\]
(16)

\[x = 1 + x_1 - x_2\]
(17)

where \( t \) is the time, parameter \( k_1 \) is the kinetic rate constant for thermal regeneration of entanglements, \( k_2 \) is the kinetic rate constant for the destruction of entanglements, \( x_1 \) denotes untangling density, \( x_2 \) denotes tangling density, \( x \) denotes entanglement density, which is a set of scalar structural variables, each ranging from 0 to 1. \( \lambda = \lambda_0 \left( \frac{x + \alpha}{1 + \alpha} \right)^{1/4} \), where \( \lambda \) is the relaxation time, \( \lambda_0 \) is the equilibrium values of \( \lambda \), and \( \alpha \) is a constant parameter.

Therefore, the change of the entanglement density describes as following:

\[
\frac{dx}{dt} = \frac{dx_1}{dt} - \frac{dx_2}{dt} = k_1 \frac{1}{\lambda} \left( 1 - x \right) - k_2 \left( \frac{\Delta P \cdot r}{2KL} + \frac{\sigma E}{K} \right)^{1/n} x
\]

\[
= \frac{k_1}{\lambda_0 \left( \frac{x + \alpha}{1 + \alpha} \right)^{1/4}} \left( 1 - x \right) - k_2 \left( \frac{\Delta P \cdot r}{2KL} + \frac{\sigma E}{K} \right)^{1/n} x
\]

(18)

It is obvious that the equation (18) is non-linear and has no analytic solution, so the numerical solution of it can be obtained by using Runge-Kutta fifth-order ordinary differential equation solver.

4. Conclusion
In this work, the theoretical framework is developed to describing the physical mechanisms of polymer melts in the electric field, from analysis, the viscosity and the elasticity of the polymer melts in the electric field are both decreased, and the relationship between the entanglement density and the voltage is established, which can be helpful for the polymer processing.

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