

RHEOLOGICAL PROPERTIES OF POLY(VINYLIDENE FLUORIDE) IN MOLTEN STATE*

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Abstract The rheological behavior of poly(vinylidene fluoride) (PVDF) samples of different molecular weights was investigated by means of high pressure capillary rheometer and rotational rheometer. Information on the rheological properties of such materials above melt temperatures is of interest as this can lead to an improved understanding of polymer behavior in processing and fabrication technologies. Shift factors derived from time-temperature superposition showed good fit to the Arrhenius equation with a flow activation energy E of almost 74 kJ/mol, which was essentially independent of polymer molecular weight suggesting the unit of flow was a collective motion of chain segments rather than the whole chain itself.

Keywords: Poly(vinylidene fluoride); Rheological properties; Flow activation energy; Plateau modulus.

INTRODUCTION

With remarkable chemical, electrical, mechanical and easy processing properties, based on which poly(vinylidene fluoride) (PVDF) was known for its potential for technical applications, PVDF has been used widely in all kinds of shapes^[1]. As a semicrystalline polymer containing crystalline and amorphous and/or rubbery phase, its crystalline phase provides thermal stability while the latter provides the desired membrane flexibility. PVDF membranes have been applied and studied widely^[2–11]. PVDF and its copolymers with other fluorocarbons were well known to have ferroelectric, piezoelectric and pyroelectric properties^[12, 13]. So they have been increasingly used in devices as sensors, transducers and actuators for different purposes.

The rheological properties studied are capillary flow properties including the flow curve and dynamic viscoelasticities such as complex viscosity, zero shear viscosity, storage modulus, and loss modulus which depend on the molecular structure of the polymeric material. But little attention has been paid to the rheological properties in molten state for PVDF. Carrot has presented a calculation of the dynamic moduli from the molecular weight distribution of PVDF^[14]. Gonnet has performed the simultaneous dielectric and dynamic mechanical measurements on PVDF in the molten state^[15]. In the present paper, we will focus on the rheological properties of PVDF melts and their dependence on temperature and molecular weight, from which we can obtain the flow activation energy E of PVDF melts and its entanglement molecular weight M_e . The rheological behavior over a wider range of shear rates (10^{-2} – 5×10^3 s⁻¹) for PVDF melt was investigated by means of high pressure capillary rheometer and rotational rheometer. Such data are of great interest not only in quality control, but also in designing suitable processing conditions.

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EXPERIMENTAL

The materials selected were two commercial resins of poly(vinylidene fluoride) (PVDF) manufactured by Solvay Solexis, Inc. (France). The molecular characteristics of both PVDF resins are listed in Table 1. The molecular weight (M_w) and molecular weight distribution were measured by gel permeation chromatography (GPC, PL-220, Polymer Laboratories Ltd., England) with μ -Styragel columns using tetrahydrofuran as an eluant (1 mL/min) and polystyrene standards. Both resins have very similar molecular weight distributions and M_w of PVDF2 is higher than that of PVDF1.

Table 1. Average molecular weights determined by gel-permeation chromatography

Samples	PVDF1	PVDF2
$M_w (\times 10^3)$	125	170
$M_n (\times 10^3)$	45	59
M_w/M_n	2.78	2.88

The melt rheological behavior of the both PVDF resins was characterized by a high pressure capillary rheometer (Thermal Haake, Germany) and an advanced rheological extension system (ARES) (Rheometrics, USA). Steady shear flow measurements were performed on the high pressure capillary rheometer in a shear rate range between 100 and 5000 s^{-1} and the rotational rheometer in steady mode in a shear rate range of 0.01–10 s^{-1} . A capillary with diameter of 1 mm in and length/diameter (L/D) ratio of 40 was used. The effects of temperature were studied at 200, 220, 240, and 260°C for all resins. Oscillatory shearing flow properties were measured using ARES. The resins were first compression molded into disk-like samples at 200°C. These resins were subsequently quenched to ambient temperature and stamped out of the molded slabs. The diameter and thickness of the disk-like samples were 25 mm and 1.2 mm, respectively. The measurements were performed in a frequency range between 0.01585 rad/s and 10 rad/s at 200, 220, 240, and 260°C for all resins. The strain was set at 0.5%, which belongs to the linear viscoelastic region, located by the aid of previous amplitude sweeps.

RESULTS AND DISCUSSION

Viscosity (Flow Curve)

Figure 1 shows flow curves in a wide shear rate range, which were obtained as the viscosities from rotational rheometer in steady mode and as the steady-state viscosities from capillary flow properties, at various temperatures for PVDF1 sample. According to the empirical rule of Cox-Merz, the complex viscosity $|\eta^*(\omega)|$ from oscillatory shear rheology equals steady shear viscosity $\eta_a(\dot{\gamma})$ for equal values of ω and $\dot{\gamma}$, which is well applicable to ordinary polymer melt and solutions^[16]. Figure 1 shows that at very low shear rates, PVDF melt exhibits Newtonian flow behavior, where apparent viscosity η_a remains at η_0 almost independent of shear rate. However, it shows non-Newtonian flow behavior with marked shear thinning at higher shear rates.

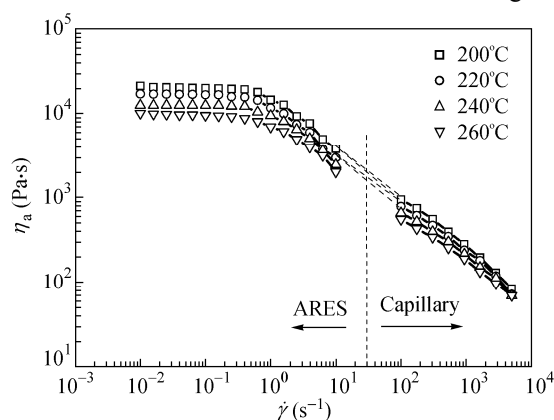


Fig. 1 Apparent viscosity as a function of shear rate for melt of PVDF1 at various temperatures

As shown in Fig. 2, the reduced apparent viscosity η_a/η_0 can be superposed to construct a master curve of flow by shift the data along the shear rate axis. The master curve can be well described using the Carreau model^[17]

$$\eta_a = \frac{\eta_0}{\left[1 + (t_c \dot{\gamma})^2\right]^{\left(\frac{1-n}{2}\right)}}$$

where t_c is a characteristic time and n is an exponent. Data fitting gives $n = 0.4$ being independent of temperature. The characteristic time t_c is determined as 1.50, 1.35, 1.12 and 0.90 s for the melt at 200, 220, 240 and 260°C, respectively.

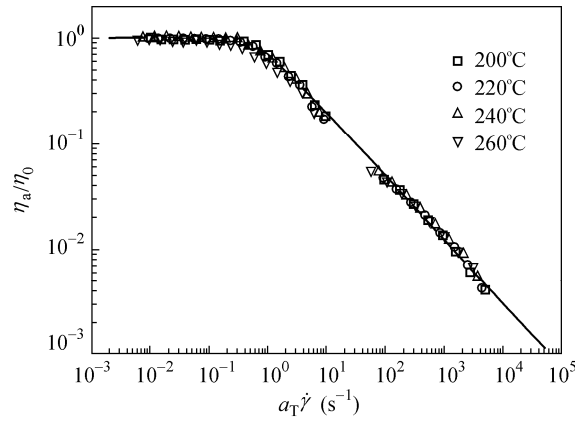


Fig. 2 Master curve of reduced apparent viscosity at 200°C for melt of PVDF1

The temperature dependence of the apparent viscosity η_a can be well described by the Arrhenius relation

$$\ln \eta_a = \ln A + \frac{E}{RT}$$

where A is a materials constant, R is the universal gas constant and E is the flow activation energy. The plots of $\ln \eta_a$ versus $1/T$ at different shear rates for PVDF1 are shown in Fig. 3. A pretty good linearity for all curves is observed, reflecting that the relationship between $\ln \eta_a$ and $1/T$ obeys the Arrhenius form. The flow activation energy E at a constant shear rate can be determined from the slope of the line by performing the least square fit to the plots. The values of E at various shear rates are listed in Table 2. One can observe that the viscous

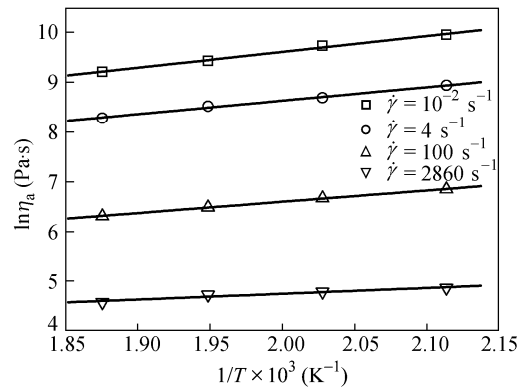


Fig. 3 Determination of flow activation energy of PVDF1 at constant shear rate

activation energy E reduces with the increase in the shear rate. The melt fluidity of polymer is related to the structure and free volume. The increase in temperature may result in the enhancement of free volume and improvement of chains mobility, and thus may strengthen the melt fluidity and decrease the apparent viscosity exponentially. The value of E reflects the temperature-sensitivity of the apparent viscosity. The higher the E is, the stronger temperature-sensitivity of the apparent viscosity is. The data in Table 2 indicate that the temperature-sensitivity of apparent viscosity of PVDF becomes faded with the shear rate increasing. That is to say, the melt fluidity of PVDF is stable over a wider temperature range at a given shear rate and ensures the easy processing of PVDF.

Table 2. Values of E of PVDF1 at different shear rate

$\dot{\gamma}$ (s^{-1})	0.01	4	100	2860
E (kJ/mol)	25.8	22.5	18.9	9.7

Plateau Moduli

Figure 4 shows the master curves of storage modulus G' , loss modulus G'' and complex viscosity η^* as a function of oscillation frequency ω at 200°C. Good data composition is obtained at $\omega > 0.1 \text{ rad s}^{-1}$ while considerably scattering in G' is observed at low frequencies. The data scattering at low frequencies is due to the thermal oxidation that introduces crosslinking of PVDF macromolecules. Wu *et.al.* found that the thermal oxidation of HDPE introduces a G' plateau at the low frequency region^[18]. In the lower frequency region the holding time was longer. Crosslinking took place within HDPE under the effect of oxygen and high temperature.

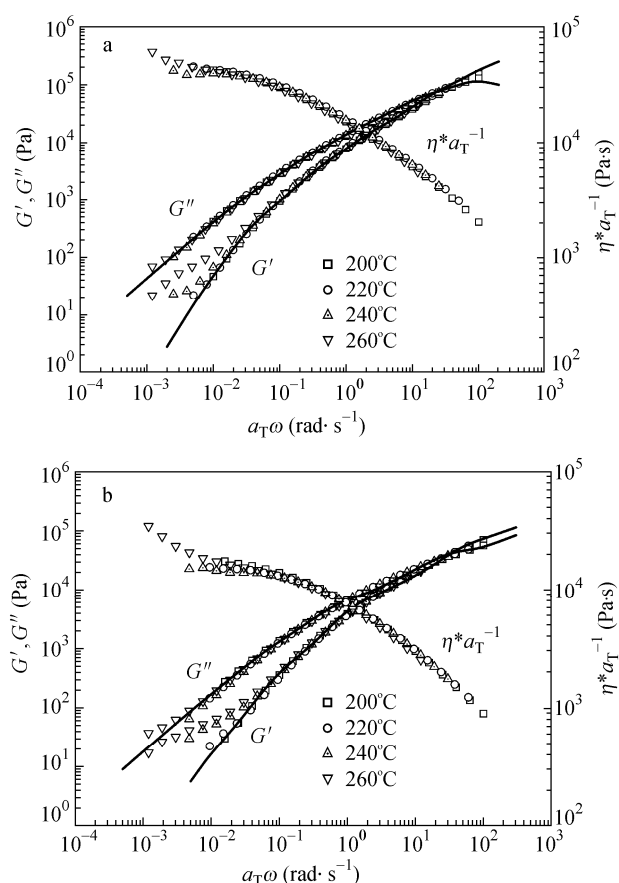


Fig. 4 Master curves for PVDF1 (a) and PVDF2 (b) melt at 200°C. The data are measured at 200, 220, 240 and 260°C, respectively.

It induced the deviation of G' from linearity. As shown in Fig. 4, G' at $\omega < 0.1 \text{ rad s}^{-1}$ increases with increasing temperature. At the same time η^* at low frequencies does not remain constant but increases with decreasing frequency. Comparing with HDPE the crosslinking reaction seems to be more important than degradation for PVDF at low frequencies.

Neglecting the thermal oxidation at 200°C , G' and G'' are fitted to the generalized Maxwell model^[19]

$$G' = \sum_i G_i \frac{\omega^2 \tau_i^2}{1 + \omega^2 \tau_i^2}$$

$$G'' = \sum_i G_i \frac{\omega \tau_i}{1 + \omega^2 \tau_i^2}$$

where G_i and τ_i are modulus and relaxation time of the i th relaxation mode. The best fitting with $i = 6$ is shown as solid curves in Fig. 4. The plateau moduli estimated through

$$G_N^0 = \sum_i G_i$$

are 0.27 MPa and 0.31 MPa for PVDF1 and PVDF2, respectively, which give rise to entanglement molecular weight of 24000 and 21000, respectively. These values of entanglement molecular weight obtained are in close agreement with that ($M_e = 22700$) reported by Krevelen^[20]. The value of M_e was found to be approximately half the value of the average critical length of the chains in order to form entanglements with other chains (M_c), so here the M_c values were found to be 48000 and 42000. In this paper the M_w of both PVDF resins is greater than M_c .

The temperature dependence of the frequency shift factor a_T can be well described by the Arrhenius relation also

$$\ln a_T = \frac{E}{R} \left(\frac{1}{T} - \frac{1}{T_s} \right)$$

where R is the universal gas constant, T_s is a referent temperature and E is the activation energy for viscous flow. Figure 5 shows a_T as a function of $1/T$ in a semilogarithmic plot. The activation energy for viscous flow E of PVDF is determined as about 74 kJ/mol, which is close to the value reported by Wu *et al.*^[21]. Consequently the flow behavior of a PVDF melt can be calculated for all temperatures within the experimental temperature range considered. The activation energy for viscous flow was found to be essentially independent of molecular weight suggesting that, for polymers of M_w greater than M_c , the unit of flow must involve a collection of chain segments,

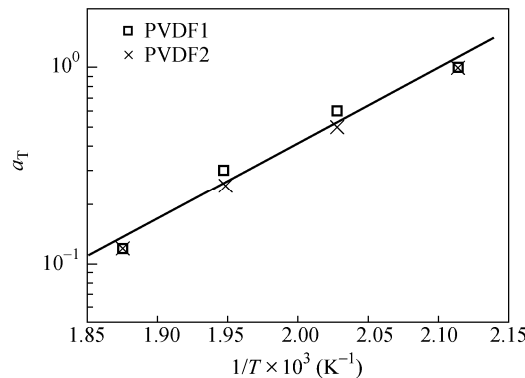


Fig. 5 Arrhenius plot to determine the flow activation energy of PVDF melts

rather than the whole chain itself. These observations are in close agreement with those reported by Masuda *et al.*^[22]. They found that the shift factor was independent of molecular weight provided that the molecular weight M_w greater than M_c , while for the polymers of lower molecular weight, the behavior was highly sensitive to polymer molecular weight. The activation energy for viscous flow reflects the sensitivity of molecular relaxation to temperature while the flow activation energy in Table 2 reflects the sensitivity of viscosity to temperature.

CONCLUSIONS

The rheological characteristics over a wider range of shear rates (10^{-2} – $5 \times 10^3 \text{ s}^{-1}$) in molten state for PVDF samples with similar molecular weight distribution but different molecular weights were investigated by means of high pressure capillary rheometer and advanced rheological extension system.

(1) The changing trend of the flow curves for both samples was similar which shows that in very low shear rates range, PVDF melts showed Newtonian flow behavior but non-Newtonian flow behavior in higher shear rates range.

(2) The temperature dependence of the shift factors could be well described by the Arrhenius relation, from which the flow activation energy of both samples was found to be around 74 kJ/mol without essential difference.

(3) The plateau moduli have been obtained by fitting the dynamic data to the generalized Maxwell model. The entanglement molecular weights estimated through plateau modulus are in close agreement with what were reported.

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