Isothermal Melt Crystallization Kinetic Behavior of Poly (vinylidene fluoride)

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Abstract

Isothermal melt crystallization kinetics of PVDF was investigated by differential scanning calorimetry. Thin PVDF film has been fabricated by the solvent casting technique using dimethylformamide (DMF). Then, the samples were melted and subsequently crystallized in the range of the crystallization temperature (T_c) between 138 and 145 °C. The crystallization kinetics was derived from Avrami equation. Avrami parameter (n) was found in a range from 1.5 to 2.4 and the values of the crystallization rate parameters (k) increased with decreasing T_c. So the crystallization rate parameters suggested that PVDF crystallize slower with increasing of T_c. The Hoffman–Weeks equation has used to approximate the equilibrium melting point of PVDF which was concluded to be 182 °C. Likewise, the activation energy was estimated to be 103.2 kJ/mol for isothermal crystallization. In this research, Lauritzen- Hoffmann theory was employed to analyze crystallization kinetics. Accordingly, regime "I" found appropriate to describe the present case of PVDF crystallization.

Introduction

PVDF as a semi-crystalline polymer is widely used in industrial fields. Its macroscopic properties are governed by the crystallization, structure and microscopic morphology [1-3]. PVDF crystallinity degree is approximately fifty percent. Four different phases known as α, β, γ and δ are exhibited as crystalline structure of PVDF. The α and β-phases are the most important crystalline polymorphs. The crystalline phases of PVDF are changed by processing condition such as synthesis conditions, method of casting, stretching of thin films and annealing conditions [4]. Therefore, it is important to study crystallization kinetics to predict crystal properties suitably, and to understand and control the crystallization process [1-3].

PVDF with excellent physical and chemical properties has been used for various applications such as acoustics, ultrasound and biomedicine fields [5-8]. Ferroelectric properties of PVDF have been studied in the last three decades [9]. Evaluation of crystallization kinetics of PVDF is of great importance in polymer processing, due to the fact that its physical properties are strongly dependent on the final morphology and the extent of crystalline phase [8]. Thermal analysis methods such as differential scanning calorimetry (DSC) are broadly used to follow the evolution of crystallization [10-11]. Initial crystal nucleation and the final crystal growth are two phenomena to examine the overall crystallization kinetics. Isothermal crystallization method is identified to obtain kinetics data based on quickly cooling the polymer sample from the melt to the crystallization temperature and then evaluate the heat evolved as the polymer sample is held isothermal. The Avrami model was applied to describe the isothermal crystallization data [12].

Many factors such as average molecular weight, molecular weight distribution, nucleating agent, and presence of plasticizers or other additives affect the isothermal crystallization [13-16]. Researchers have widely investigated the crystallization behavior of PVDF and blends based on PVDF. Yu *et al*. [17]

employed the Avrami approach modified by Jeziorny to successfully illustrate the non-isothermal crystallization process of PVDF/montmorillonite (MMT) composite. They have found that the crystallization temperature of PVDF/MMT nanocomposite was higher than that of PVDF at various cooling rates.

Qiu et al. [18] have studied spherulitic morphologies and overall crystallization rate kinetics of miscible poly(vinylidene fluoride)/poly(butylene succinate-*co*-butylene adipate) (PBSA) blends. They found that the crystallization mechanism does not alter for the high-T_m component PVDF, although both the spherulitic growth rate and the overall crystallization rate of PVDF are reduced with increasing crystallization temperature and the PBSA content in the blends.

Chiu [19] has studied the spherulitic morphology and crystallization kinetics of the blends of poly(vinylidene fluoride) and poly(vinyl acetate) (PVAc). They found that both the PVDF spherulitic growth rate and the overall crystallization rate constant (k_n) were depressed with either the adding of PVAc or the increasing of crystallization temperature. The kinetics retardation was ascribed to the decrease in PVDF molecular mobility and dilution of PVDF concentration due to the addition of PVAc, which has a higher glass transition temperature. By decreasing molecular mobility and dilution of PVDF concentration, which is due to the adding of PVAc, the kinetics retardation was ascribed, having a higher glass transition temperature. Fan and Zheng [20] studied the miscibility behavior in blends of poly(methyl methacrylate) and poly(vinylidene fluoride). The Avrami exponent decreases with increasing crystallization temperature. Sencadas et al. [8] studied the isothermal melt crystallization of PVDF at different crystallization temperatures. The Avrami parameters and the Hoffman-Weeks were discussed to obtain the equilibrium melting temperature. The crystallization of poly (vinylidenefluoride) / poly (3-hydroxybutyrate) (PHB) blends were studied by Liu [21]. The Avrami exponent for PVDF was smaller than that of for compact growth, showing the two-dimensional lamellar growth. Asai et al. have studied the effect of the layer titanate (HTO) as the nano-filler particles on the crystallization kinetics and crystalline structure of poly(vinylidene fluoride) (PVDF). The overall crystallization rate improved in the PVDF/layer HTO nano-composite. For both neat PVDF and PVDF/HTO crystallization, the transition from regime III to regime II was found to occur. It was considered that HTO particles are the nucleating agent [22].

Although several articles have reported the crystallization of PVDF, the kinetics needs to be investigated in details for further optimization of the overall melt crystallization properties of PVDF. This study reports on the kinetics of the isothermal melt crystallization of PVDF at different crystallization temperature by DSC. Kinetic parameters were estimated on the basis of the Avrami equation and Lauritzen- Hoffmann (LH) approach. Hoffmann- Weeks extrapolation was applied and the value of the equilibrium melting temperature was calculated. The isothermal crystallization activation energy was also calculated.

2. Experimental
2.1. Material and film preparation
PVDF films were prepared using a solvent casting method. PVDF granule (M_w=530kDa, from Sigma-Aldrich, USA) were dissolved in N, N-Dimethylformamide, DMF (from Sigma-Aldrich, USA) at 50 ºC for 10 h. The PVDF solution was poured into a flat dish for solvent evaporation at room temperature during 2 weeks. The samples were dried further at 50 ˚C for 8 h to remove the solvent residues. The thickness of polymer films were about 150-200 μm.
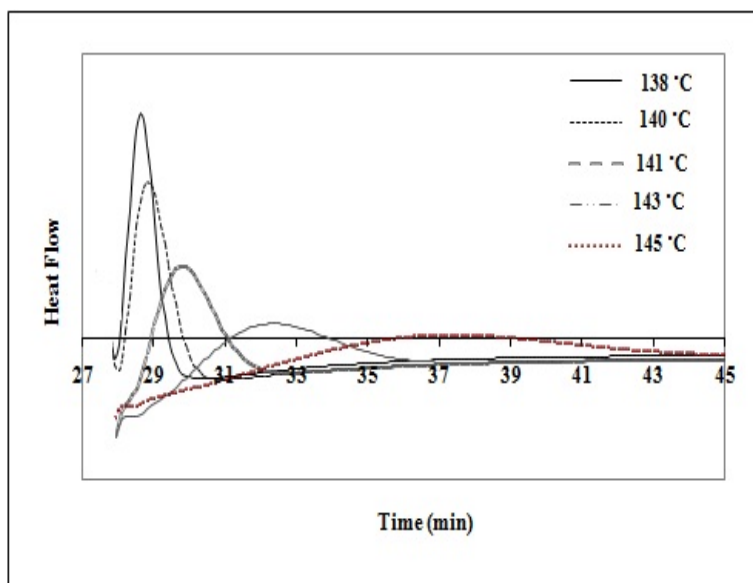
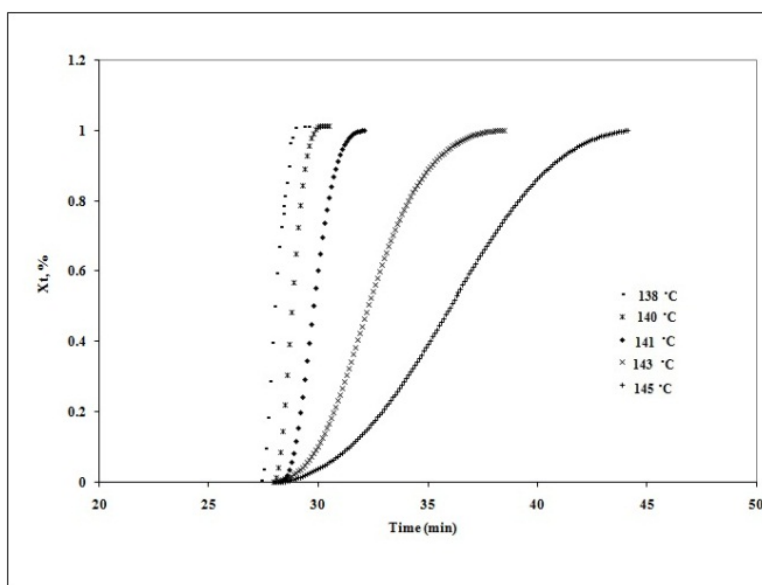**Figure 1: Isothermal melt crystallization exotherms for PVDF films**

Figure 2: The relative crystallinity as a function of time for PVDF films.

2.2. Characterization kinetics measurements

The crystallization kinetics of PVDF polymer was evaluated using a differential scanning calorimeter (DSC) (Polylabe 625, instrument, UK). The weights of all samples were ~5 mg. The samples were heated from room temperature to 220 ˚C with 10 ˚C min⁻¹ heating rate and held for 5 min to eliminate the previous thermal history. Finally, the samples were cooled (at -40 ˚C min⁻¹) to the designated crystallization temperatures, which were five different temperatures ranging from 138 to 145 ˚C.

3. Results and discussion
3.1. Isothermal Crystallization Kinetic Analysis

DSC thermograms of PVDF crystallized at different temperatures are presented in Figure 1. It is observed that the crystallization exothermic peak shifts to larger times and also peak width increases

with increasing crystallization temperature (T_c).

This fact is due to decreasing crystallization rate with increasing T_c. The bell shape of the peaks suggests a primary crystallization with no obvious secondary crystallization occurring after isothermal crystallization process. The overall crystallization kinetics is determined by the nucleation and growth rates. The relative degree of crystallinity (X_t) as a function of time can be calculated by [8]:

$$X(t) = \frac{\int_0^t \left(\frac{dH}{dt}\right) dt}{\int_0^\infty \left(\frac{dH}{dt}\right) dt} \qquad (1)$$

Where ($\frac{\partial H}{\partial t}$) is the DSC heat flow.

Figure 2 shows the evolution of the relative degree of crystallinity with time for the various crystallization temperatures. The initial slope of the isotherms decreases with increasing crystallization temperature, indicating a progressively slower crystallization rate.

The crystallization processes are usually treated as a combination of two stages: the primary crystallization stage and the secondary crystallization stage. The Avrami equation has been used to describe the primary stages of isothermal kinetics. If the relative degree of crystallinity increases with an increase in the crystallization time t, the Avrami equation (eq 2) can be used to analyze the isothermal crystallization process [23]:

$$X(t) = 1 - \exp(-kt^n) \qquad (2)$$
$$\ln[-\ln(1 - X(t))] = \ln k + n \ln t \qquad (3)$$

Where $X(t)$ is relative degree of crystallinity at time t, k and n are the crystallization rate constant and the Avrami exponent respectively, being dependent on the type of nucleation and growth process parameters. The Avrami exponent (n) and crystallization rate constant (k) can be obtained by plotting $\ln[-\ln(1 - X(t))]$ as a function of ln t, as shown in Figure. 3.

At the early state of crystallization, $\ln[-\ln(1 - X(t))]$ is in a good linear correlation with ln t. However, Avrami plots generally deviate from linear regression at the higher crystallization ratios, mainly due to the ignoring the considerable role of secondary crystallization processes. Avrami parameters are listed in Table 1.
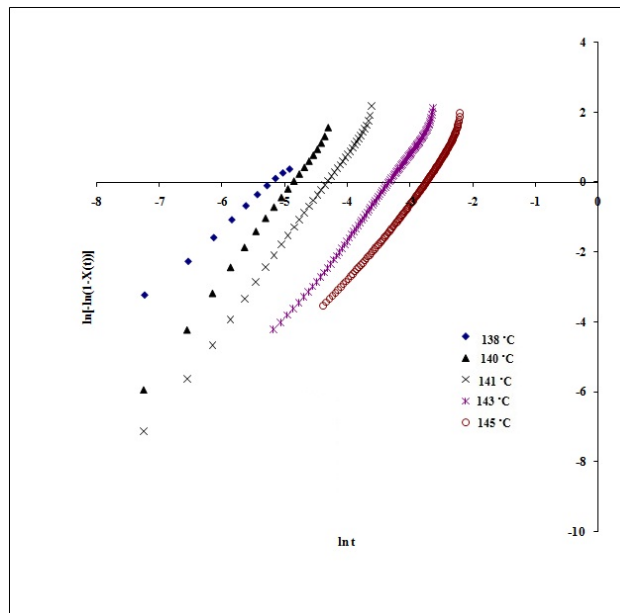

Figure 3: Plot of ln[-ln(1-X(t))] as a function of ln t for PVDF films using Avrami Model

From Table 1, it can be seen that Avrami parameter, n is in a range from 1.5 to 2.4 at the primary stage, depending on T_c. These results indicate that the nucleation and spherulite growth are free at the primary crystallization stage. The values of the crystallization rate parameter, k increase with decreasing T_c since melt crystallization depends on the temperature which is the characteristic of nucleation controlled crystallization. The crystallization half-time ($t_{1/2}$), defined as the time at which the extent of crystallization is 50% complete, is determined by the measured parameters:

$$t_{1/2} = \left(\frac{\ln 2}{k}\right)^{1/n} \qquad (4)$$

Usually, the crystallization rate (G) is described as the reciprocal of $t_{1/2}$; that is, G=$t_{1/2}$. Because the time for the maximum crystallization rate to occur (t_{max}) corresponds to the point at which dQ(t)/dt = 0, in which Q(t) is the heat-flow rate, we can use the Avrami equation to write t_{max}, obtaining the following [24]:

$$t_{max} = \left(\frac{n-1}{nk}\right)^{1/n} \qquad (5)$$

The values of k, n, and t_{max} are reported in Table 1. With an increase in T_c, the crystallization exothermal peaks shift to higher temperatures and become flat; this means that the total crystallization time is extended. It can be seen that both k and G decrease as crystallization temperature increases which indicate that PVDF crystallization becomes slower.

Table 1: Kinetic parameters for isothermal crystallization of PVDF

T_C (°C)	n	K (min⁻¹)	$t_{1/2}$ (min)	t_{max} (min)	G (min⁻¹)	U* (J/mol)
138	1.59	8.24	0.21	0.14	4.74	30977.72
140	2.49	12.16	0.31	0.29	3.15	30859.23
141	2.51	10.83	0.33	0.31	2.98	30800.76
143	2.16	7.23	0.33	0.3	2.96	30685.29
145	2.41	6.71	0.38	0.36	2.56	30571.78

3.2. Equilibrium Thermodynamic Parameters

The equilibrium melting temperature (T^0_m) is an important parameter for characterizing a given crystal of a flexible linear polymer that is not available directly, so indirect or extrapolation methods must be used. As a main approach, the Hoffman–Weeks equation has been widely used to estimate the equilibrium melting point of polymers. According to theoretical considerations by Hoffman and Weeks [25], the equilibrium melting point of polymers can be deduced from the DSC measurements by the plotting of the observed apparent T_m versus the isothermal T_c. The equilibrium melting point is obtained by means of the intersection of the resulting straight line by the line $T_m = T_c$. The dependence of T_m on T_c is given by:

$$T_m = T^0_m\left(1 - \frac{1}{2\beta}\right) + T_c\frac{1}{2\beta}$$

(6)

Where β is the lamellar thickening factor, which is the ratio of the initial to the final lamellar thickness. Under equilibrium conditions, β is equal to 1. Hoffman-Weeks plot is shown in Fig 4, and a value of 182 °C for T^0_m was obtained.

3.3. Spherulitic Growth Analysis

The thermodynamic parameters related to the crystallization process were evaluated through the regime theory of crystal growth. Hence, the temperature dependence of the linear growth rate (G) as the Lauritzen-Hoffman equation is given as [26]:

$$G = G_0 \exp\left(\frac{-U*}{R(T_C - T_\infty)}\right)\exp\left(\frac{-K_g}{fT_C\Delta T}\right) \qquad (7)$$

where G_0 is a pre-exponential term, U* is the diffusion activation energy for transport of where $U*$ is the transport activation energy, T_∞ is a hypothetical temperature below which all viscous flows cease and is related to T_g ($T_\infty = T_g$ _ 30 K), ΔT (T^0_m _ Tc) is the degree of super cooling, K_g is a nucleation parameter, and f is a correction factor accounting for the variation in the bulk melting enthalpy per unit volume with temperature [$f = 2T_c/(T^0_m$ _ T_c)].

The transport term $U*$ can be calculated with the Williams–Landel–Ferry relation [27]:

$$U* = \frac{C_1 T_c}{C_2 + T_c - T_g} \qquad (8)$$

Where C_1 and C_2 are constants (generally assumed to be 4120 cal/mol and 51.6 K, respectively) [24].The values of $U*$ are listed in Table 1. It is convenient to rearrange as:

$$\ln G + \frac{U*}{R(T_C - T_\infty)} = \ln G_0 - \frac{K_g}{f T_C \Delta T} \qquad (9)$$

The plot of $\ln G + U*/R(T_c - T_\infty)$ versus $1/(f T_c \Delta T)$ should yield a straight line with $-K_g$ as the slope (Figure. 5), and K_g was determined to be $1.4 * 10^5$ K2 for PVDF.

Parameter K_g can be used to refer the crystallization regime of polymers and calculate the lateral interfacial free energy (σ) and interfacial free energy of chain-folded surface (σ_e) from the following equations [28]:

$$K_g(I) = \frac{4 b_0 (\sigma \sigma_e) T_m^0}{\Delta h_f^0 . k} \quad or \quad K_g(II) = \frac{2 b_0 (\sigma \sigma_e) T_m^0}{\Delta h_f^0 . k} \qquad (10)$$

Where b_0 is the thickness of a monolayer and Δh_f^0 is the bulk melting enthalpy per unit volume for 100% crystalline polymer ($\Delta h_f^0 = \Delta H_m^0 \times \rho_c$). K_g is equal to K_g (I)

when the formation of a surface nucleus is followed by fast completion of substrate (regime I kinetics, rate of surface nucleation is smaller than rate of chain diffusion), and K_g is equal to K_g (II) when the surface nuclei forms in large numbers on the substrate and diffuses slowly (regime II kinetics, rate of surface nucleation is roughly equal to rate of diffusion).

To confirm the regime of the crystallization kinetics, the Lauritzen Z test is applied [29]:

$$Z \cong 10^3 \left(\frac{L}{2 a_0}\right)^2 \exp\left[-\frac{X}{T_c . \Delta T}\right] \qquad (11)$$

where L is the effective lamellar thickness and a_0 is the width of the molecular chain in the crystal. Regime I occurs when Z smaller than or equal to 0.01(with replacement of $X = K_g$) and regime II occurs when Z greater than or equal to 1.0 (with replacement of $X = 2 K_g$) [25]. For PVDF, a, b and c as the lattice parameters are reported 4.96, 9.64 and 4.62 Å, respectively [1]. Also, if the special crystal growth is on the 100 planes, as a result a_0 is 4.82 Å and b_0 is 4.96 Å. In this study, if $Z \leq 0.01$ and $X = K_g$, L will be smaller than 14.4 Å: this result being reasonable for polymers. On the other hand, if Z is greater than or equal to1 and $X = 2 K_g$, we obtain $L \geq 686.8$ Å, this result is not realistic. Therefore, regime I is take placed for PVDF.
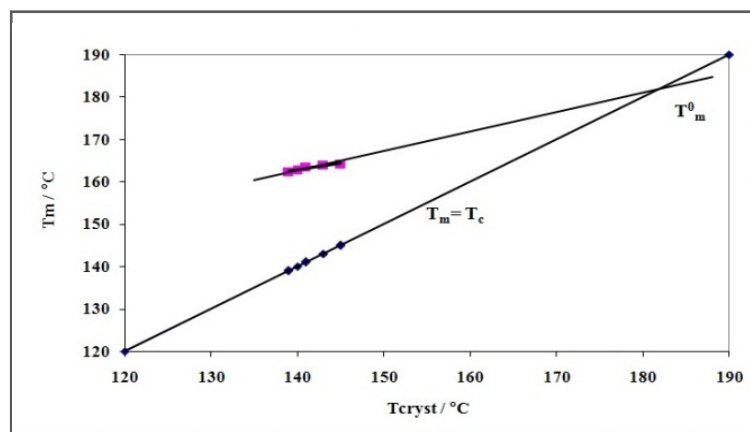

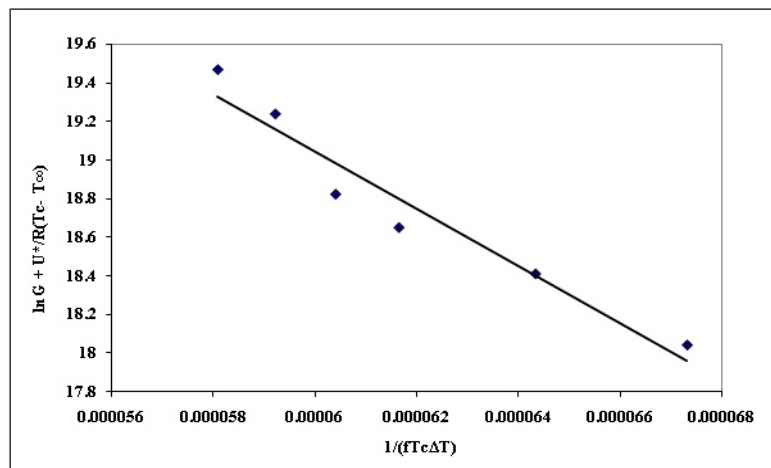**Figure 4: Application of the Hoffman–Weeks approach to PVDF**
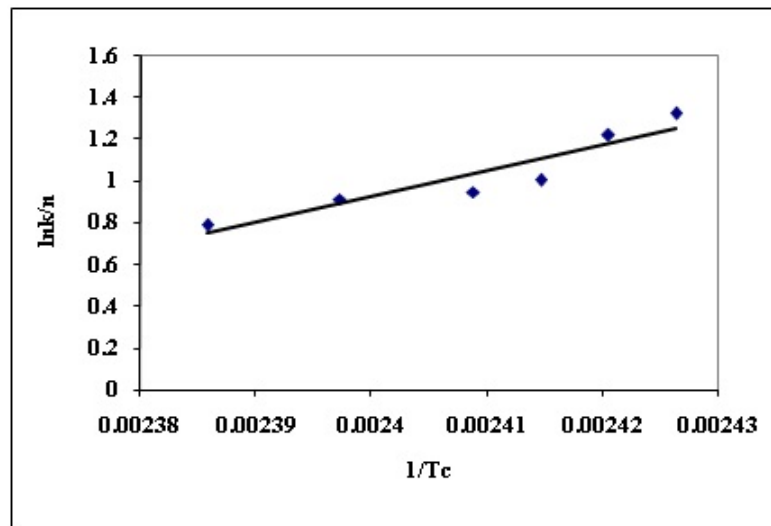
Figure 5: The plot of lnG +U*/R(Tc- T∞) versus 1/(fTcΔT)

Figure 6: The plot of ln K/n versus 1/Tc

3.4. Crystallization Activation Energy (ΔE)

It is assumed that the isothermal crystallization process of PVDF is thermally activated; therefore, K can be approximately described by the Arrhenius equation [30]:

$$K^{1/n} = K_0 \exp\left(-\frac{\Delta E}{RT_c}\right) \quad (12)$$

$$\frac{\ln K}{n} = \ln K_0 - \frac{\Delta E}{RT_c} \quad (13)$$

Where K_0 is a temperature-independent pre-exponential factor and R is the gas constant. ΔE for the isothermal melt crystallization of PVDF was determined to be 103.2 kJ/mol from the slope of the plot of ln K/n versus 1/Tc (Figure 6).

4. Conclusion

A study of the isothermal meltcrystallization kinetics of PVDF was performed with DSC in the range of T_c between 138 and 145 °C. The results indicate that the Avrami equation can describe the primary stage of crystallization process. The Avrami exponent was found to be in the range from 1.5 to 2.5. All the crystallization rate parameters (i.e. $t_{1/2}^{-1}$, G) suggested that PVDF crystallize slows down with increasing of Tc. The value of

the equilibrium melting temperature $T_m^0 = 182$ °C was estimated based on the linear HW extrapolated. The crystallization regime of PVDF was confirmed to be regime I according to the Lauritzen-Hoffman equation and Z test.

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