

Crystallization Kinetics of Poly(Vinylidene Fluoride) and Poly(Methyl Methacrylate) Blend

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Abstract: The isothermal and non-isothermal crystallization kinetics of poly(vinylidene fluoride) from the blends of poly(vinylidene fluoride) and poly(methyl methacrylate) were investigated for all samples of different blend ratios at various crystallization temperatures by differential scanning calorimetry technique. The overall rates of crystallization and the kinetic crystallizability were analyzed by the Avrami relation and Ziabicki's approximate theory respectively. It was found that the Avrami constant K and the kinetic crystallizability G decreased considerably with increasing PMMA content, which suggested that the crystallization rate decrease with the increase of PMMA content in both isothermal and non-isothermal condition. The Avrami exponent n decreased slightly with increasing PMMA content although it remained constant at different crystallization temperature.

1. INTRODUCTION

Crystallization is an important property of polymeric material and the crystallization kinetics of isothermal process has been intensively studied for homopolymers. But a thorough understanding of the crystallization kinetics and mechanism of polymer blends is lacking.

The crystallization of a polymer can occur not only from homopolymers but also from mixtures which contain another polymer as an added ingredient. It is generally known that the added polymeric diluent does not affect the crystallization of the crystallizable polymer if the two polymers are incompatible in the blend. On the other hand, if the two polymers are compatible, the diffusion of the noncrystallizable polymer plays a very important role in the crystallization process of the

crystallizable polymer¹.

Calahorra et al.² investigated the blends of poly(methyl methacrylate) and poly(ethylene oxide). They found that the kinetic rate of crystallization of the blends decreased considerably with increasing PMMA concentration. Ong and Price³ investigated the isothermal spherulitic growth rates and the overall crystallization rates of poly(ϵ -caprolactone) from the blends of poly(ϵ -caprolactone) and poly(vinyl chloride) using an optical microscope and a density gradient column, respectively. They reported that the value of Avrami constant K decreased markedly with increasing PVC concentration and Avrami exponent n had a value in the neighborhood of 3, almost independent of the composition.

The blend of poly(vinylidene fluoride) and poly(methyl methacrylate) is one of the well-known miscible polymer systems. Although

many investigations have been performed on the miscibility⁴⁻⁹, dynamic mechanical properties¹⁰, morphology¹¹ and spherulitic growth rate of the blend system¹², the overall crystallization kinetics has not been reported.

In this study crystallization kinetics, both isothermal and non-isothermal, of poly(vinylidene fluoride) from the blends of poly(vinylidene fluoride) and poly(methyl methacrylate) are determined by differential scanning calorimetry and the effects of blend composition and crystallization temperature on the crystallization kinetics are discussed.

2. EXPERIMENTAL

2-1. Preparation of Samples

Poly(vinylidene fluoride)(M.W.=80,000) in powder form was obtained from the Polysciences Inc. (U.S.A.) and poly(methyl methacrylate) was obtained from the bulk PMMA by fractionation in methyl ethyl ketone. (Intrinsic Viscosity=2.615)

Films of PVDF and its blends with 5%, 10%, 15% PMMA were prepared from N, N-dimethylformamide(DMF) solution onto a glass surface at 60°C. The blend ratio in the mixture is reported on a weight basis. The initial concentration of each polymer in DMF was about 10g/100ml. After the film was cast, DMF was allowed to evaporate under vacuum at 60°C for two days and then slowly cooled to room temperature.

2-2. Thermal Analysis

Thermal analyses were performed using a DuPont 1090 Thermal Analyzer with a Differential Scanning Calorimetry(DSC) 910 module under nitrogen gas purging.

The thermal programs for DSC analysis are illustrated in Fig.1. Program(a) was used for measuring the melting temperature of the

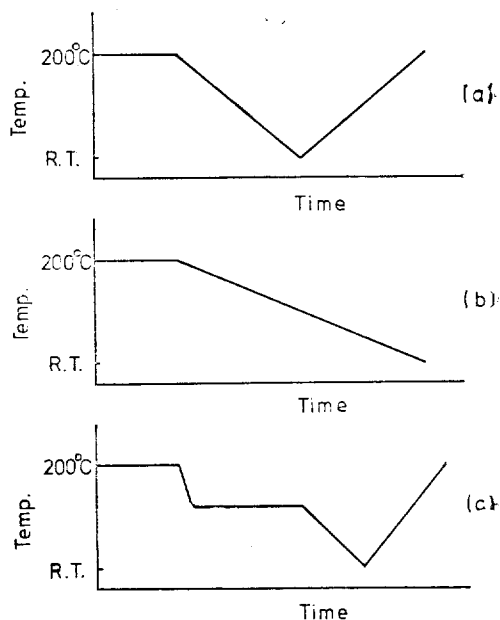


Fig. 1. Thermal programs used for differential scanning calorimetry.

samples crystallized on cooling (T_m^*). In this program the samples were maintained at 200°C for at least 15 min to ensure complete melting of the PVDF crystals, cooled to room temperature at $-20^\circ\text{C}/\text{min}$ and then heated with a rate of $20^\circ\text{C}/\text{min}$ to 200°C. Program(b) was used for determining the melt crystallization temperature. Under this program the samples were maintained at 200°C for at least 15 min and cooled with a rate of $-5^\circ\text{C}/\text{min}$. This program was also used for studying non-isothermal crystallization kinetics of the samples. For the non-isothermal crystallization, crystallization thermogram was obtained with time base. Program(c) was used for studying the isothermal crystallization of the samples. In this program the samples were heated and then rapidly cooled with a rate of $-100^\circ\text{C}/\text{min}$ to the crystallization temperature(T_{cm}), which was determined from the thermal program(b). At the crystallization temperature the samples were isothermally maintained for 10

to 30min. Following the isothermal crystallization at T_{cm} , samples were cooled to room temperature with a rate of $-20^{\circ}\text{C}/\text{min}$. In the final step of program(c) the melting temperature and heat of fusion of the isothermally crystallized samples were measured at a heating rate of $20^{\circ}\text{C}/\text{min}$.

3. RESULTS AND DISCUSSION

3-1. Isothermal Crystallization Kinetics

The melt crystallization temperature (T_{cm}) and melting temperature of the samples crystallized on cooling (T_m^*) obtained from the thermal programs (a) and (b) are given in Table 1. It is generally known that no melting point depression and crystallization temperature change of the blend are observed when the blends are incompatible. However, as shown in Table 1, results of PVDF-PMMA blend show considerable melting point depression and crystallization temperature change, which suggest that the two polymers are miscible with each other.

Table 2 shows how the melting temperature of isothermally crystallized samples (T_m), heat of fusion of pure PVDF fraction (ΔH_f°) and heat of fusion of each blend (ΔH_f) depend on the concentration of PMMA in the blends at various crystallization temperatures. Table 2 is plotted into Fig.2 to 4. As shown in Fig.3, decrease in ΔH_f which is proportional to the

Table 1. Dependence of Melt Crystallization Temperature (T_{cm}) and Melting Temperature of the Samples Crystallized on Cooling (T_m^*) on the Weight Fraction of PMMA

conc. of PMMA(%)	$T_{cm}(^{\circ}\text{C})$	$T_m^*(^{\circ}\text{C})$
0	140.3	165.9
5	139.8	165.0
10	135.1	163.8
15	132.6	161.5

Table 2. Changes in Melting Temperature (T_m) and Heat of Fusion of Blend (ΔH_f) and Pure PVDF Fraction (ΔH_f°) for Isothermally Crystallized Samples as a Function of Blend Composition and Crystallization Temperature (T_{cm})

$T_{cm}(^{\circ}\text{C})$	conc. of PMMA(%)	$T_m(^{\circ}\text{C})$	$\Delta H_f(\text{cal/g})$	$\Delta H_f^{\circ}(\text{cal/g})$
136	0	165.2	37.56	37.56
	5	165.4	33.66	35.43
	10	165.0	30.99	34.43
	15	164.2	27.45	32.29
138	0	165.6	37.90	37.90
	5	165.6	33.46	35.22
	10	165.4	30.53	33.92
	15	164.6	27.45	32.29
140	0	166.1	36.87	36.87
	5	166.0	32.66	34.38
	10	165.8	30.07	33.41
	15	165.0	26.63	31.33
142	0	166.4	37.56	37.56
	5	166.5	32.66	34.38
	10	166.1	30.07	33.41
	15	165.5	27.04	31.81

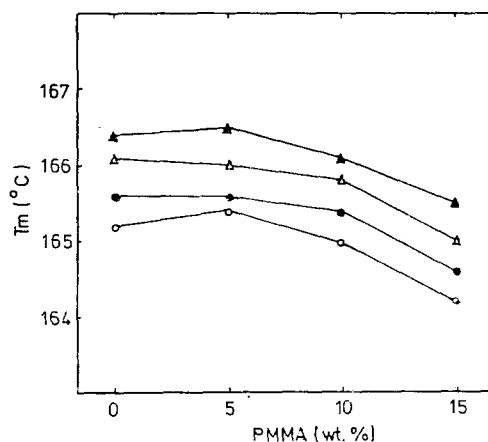


Fig. 2. Melting temperature (T_m) as a function of blend composition at various crystallization temperatures: (○) 136°C (●) 138°C (△) 140°C (▲) 142°C .

crystallinity suggests that crystallinity of the blend decrease with PMMA content because the increase in PMMA content causes the increase of amorphous fractions in the blend. If PMMA has no effect on the crystallization of

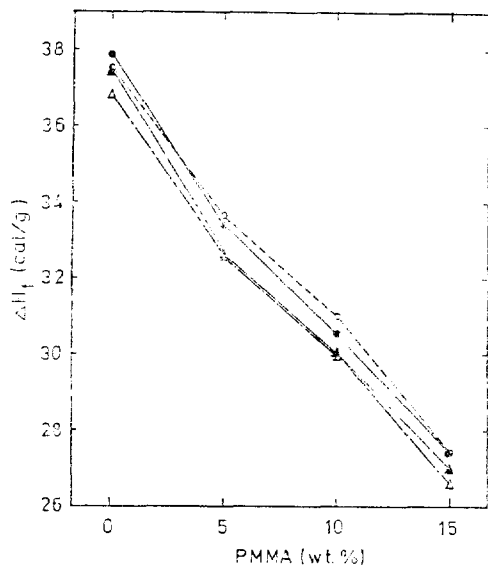


Fig. 3. Heat of fusion (ΔH_f) of blends as a function of blend composition at various crystallization temperatures: (○) 136°C (●) 138°C (△) 140°C (▲) 142°C.

PVDF, the heat of fusion for pure PVDF fraction must be constant. But, as shown in Fig. 4, ΔH_f° for pure PVDF fraction exhibits a tendency of decreasing. From these results it is tentatively suggested that PMMA have an unfavorable effect on the crystallization of PVDF in the blend.

Comparing Table 1 with Table 2, one can find that changes in T_m^* , melting temperature of the samples crystallized on cooling are comparatively larger than the changes in T_m , melting temperature of the isothermally crystallized samples. The differences are due to the annealing effect in isothermal crystallization.^{13,14} In isothermal process, which means annealing, crystallization occurs in equilibrium manner and further crystallization can be obtained. For that reason, it is considered that changes in T_m are comparatively small.

The isothermal crystallization kinetics at various crystallization temperatures was determined from the crystallization thermograms

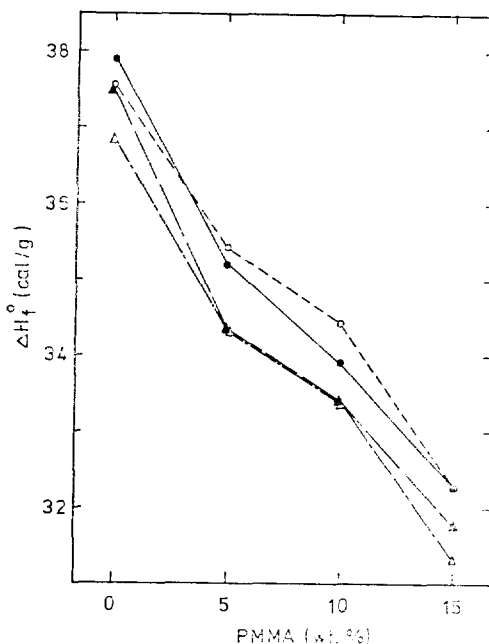


Fig. 4. Heat of fusion (ΔH_f°) of pure PVDF fraction in blends as a function of blend composition at various crystallization temperatures: (○) 136°C (●) 138°C (△) 140°C (▲) 142°C.

in program(c). Examples of such curves are reported in Fig. 5. The weight fraction X_t of material that has been crystallized at time t was calculated from the crystallization thermogram by assuming^{15,16}

$$X_t = \int_0^t (dH/dt) dt / \int_0^\infty (dH/dt) dt \dots \dots \dots (1)$$

where, the integration in equation (1) means the area of the crystallization thermogram between crystallization zero time and an arbitrary time t .

The half-time $t_{1/2}$ of conversion of PVDF from amorphous to crystalline polymer at various crystallization temperatures was determined from the crystallization isotherms.

The kinetics of isothermal crystallization was analyzed by means of the Avrami equation¹⁷

$$1 - X_t = \exp(-Kt^n) \dots \dots \dots (2)$$

where, K is the kinetic rate constant and n

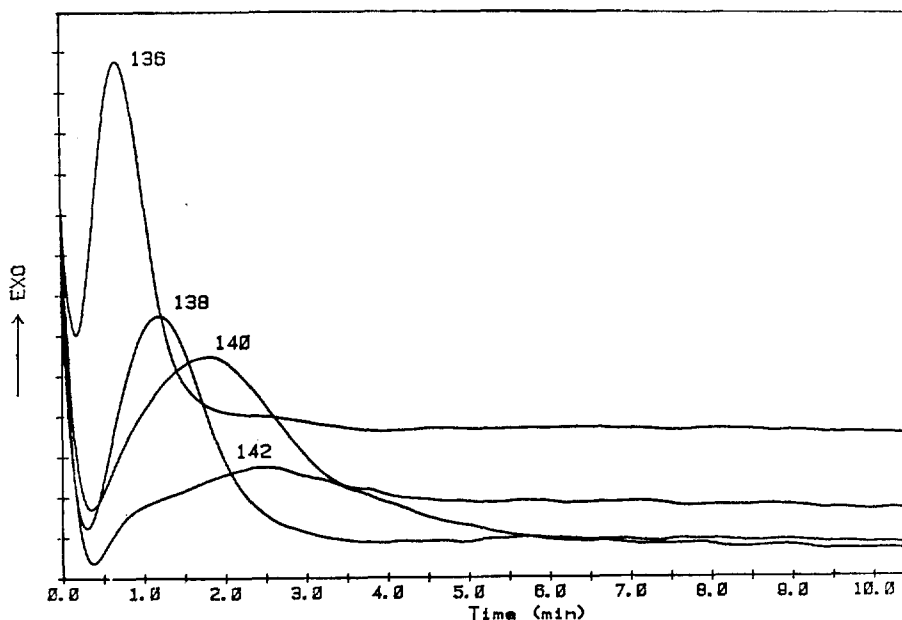


Fig. 5. Typical DSC thermograms of isothermal crystallization obtained from 10% PMMA blend.

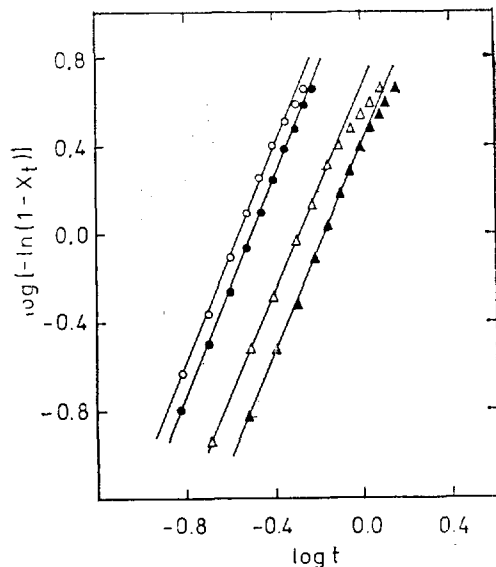


Fig. 6. Avrami plots for pure PVDF at various crystallization temperatures: (○) 136°C (●) 138°C (△) 140°C (▲) 142°C.

is the Avrami exponent. Accordingly,

$$\log[-\ln(1-X_t)] = n \log t + \log K \quad (3)$$

Avrami plots of the blends are reported in Fig. 6 to 9. Straight lines which represent the

primary crystallization are obtained for all the cases examined. From the slopes of these straight lines n was estimated.

The kinetic rate constant K was calculated by the relation;

$$K = \ln 2 / t_{1/2}^n \quad (4)$$

The values of n , K , and $t_{1/2}$ for each T_{cm} and blend ratio are listed in Table 3. Fig. 10 is the plot of $t_{1/2}^{-1}$ vs PMMA content. As can be seen in Table 3, the crystallization rate depends strongly on temperature showing a large negative temperature coefficient for each component. Such a negative temperature coefficient reveals that the crystallization is a nucleation-controlled process. As shown in Table 3 and Fig. 10, the kinetic rate constant K decreases markedly with the addition of PMMA. In other words, the half-time of crystallization $t_{1/2}$, which is frequently taken as a measure of the overall rate of crystallization, increases from 0.275 min to 1.7 min at $T_{tm}=138^\circ\text{C}$ as the composition of PMMA increases from 0 to 15 weight percent. These results are in accord

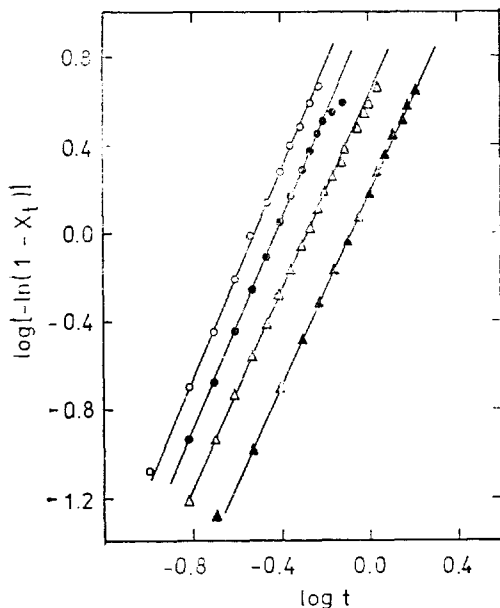


Fig. 7. Avrami plots for 5% PMMA blend at various crystallization temperatures: (○) 136°C (●) 138°C (△) 140°C (▲) 142°C.

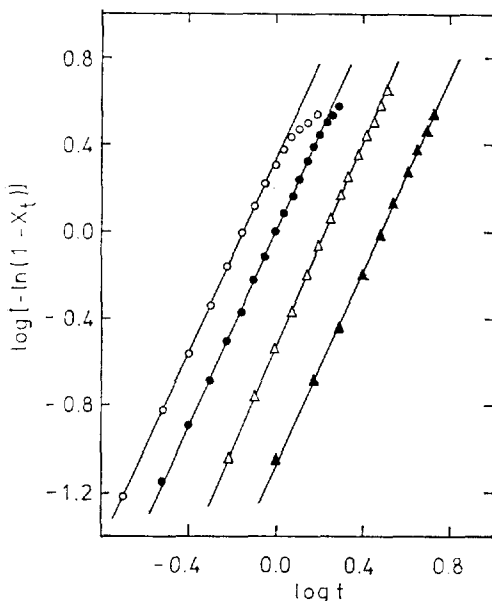


Fig. 8. Avrami plots for 10% PMMA blend at various crystallization temperatures: (○) 135°C (●) 138°C (△) 140°C (▲) 142°C.

with the previously reported miscible blend systems^{2,3} and the general theory of the spherulitic growth rate of miscible crystalline-

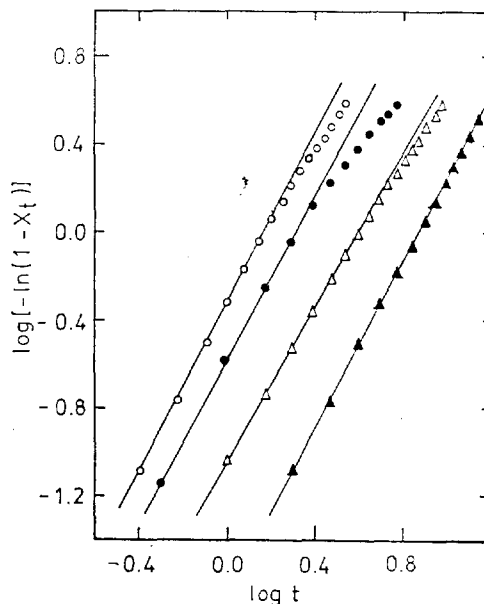


Fig. 9. Avrami plots for 15% PMMA blend at various crystallization temperatures: (○) 136°C (●) 138°C (△) 140°C (▲) 142°C.

amorphous polymer blend which has different T_g ¹⁸. The crystallization rate process is governed by the degree of supercooling or driving force and the resistance to segmental motions. Hence crystallization at finite rates is limited to the region between T_m and T_g . Elending two polymers can have an important effect on this temperature gap ($T_m - T_g$) available for crystallization. Here we consider two cases, i.e., a case where T_g increases upon adding the second component, and the other one where T_g decreases upon adding the second one. The former one will retard molecular motions, decrease the gap ($T_m - T_g$), and in general tend to restrict crystallization. For the latter one, the gap ($T_m - T_g$) is broadened, molecular motion is easier, and crystallization may become more rapid¹⁹. Previous studies revealed that T_g of PMMA was much higher than that of PVDF and that T_g of their blend was located between them. Therefore, it is reasonable

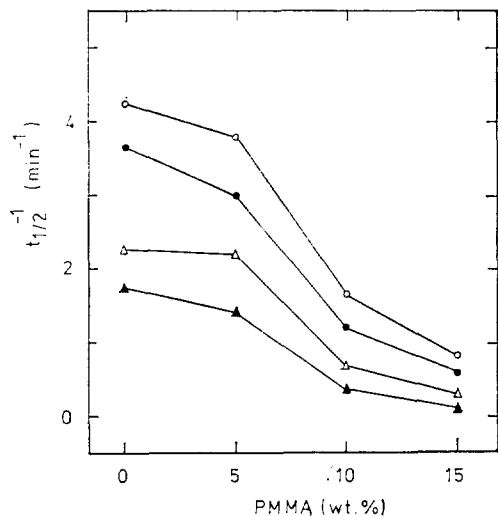


Fig. 10. Reciprocals of crystallization half-time ($t_{1/2}^{-1}$) as a function of blend composition at various crystallization temperatures: (○) 135°C (●) 138°C (△) 140°C (▲) 142°C.

to state that the former case is applicable to PVDF-PMMA blend system and hence the rate of crystallization decreases with the fraction of PMMA^{4,5,11}.

The spherulitic growth rate studies presented by Wang and Nishi¹² may be supporting evidences of the phenomenon. They found that radial growth rates of spherulites in blends of PVDF and PMMA were found to fall by as much as two orders of magnitude as the weight fraction of PMMA is increased from 0 to 50%. They explained that the factors which could give rise to such a marked composition dependence included the presence of depletion layers at growth fronts, melting point depression, and the large variation in T_g due to changes in composition. Their results can support the decrease in the overall rate of crystallization with the addition of PMMA.

As can be seen in Table 3, the Avrami exponent n is indicative of the growing mechanism of nuclei and the large values of n indicate

Table 3. Changes in Avrami Exponent (n) and Crystallization Half-Time ($t_{1/2}$) and Kinetic Rate Constant (K) of Isothermally Crystallized Samples as a Function of Blend Composition and Crystallization Temperature (T_{cm})

T_{cm} (°C)	conc. of PMMA(%)	n	$t_{1/2}$ (min)	K (min ⁻ⁿ)
136	0	2.44	0.237	23.25
	5	2.36	0.263	16.21
	10	2.21	0.600	2.14
	15	1.86	1.200	0.49
138	0	2.54	0.275	18.40
	5	2.31	0.334	8.73
	10	2.19	0.830	1.04
	15	1.83	1.700	0.26
140	0	2.36	0.440	4.81
	5	2.21	0.450	4.05
	10	2.29	1.425	0.31
	15	1.69	3.200	0.01
142	0	2.31	0.575	2.49
	5	2.15	0.700	1.49
	10	2.16	2.600	0.09
	15	1.95	6.100	0.02

higher dimensional growth and vice versa. From the results in n values, it can be tentatively assumed that the growth dimension becomes lower as the addition of PMMA. But the dependence on T_{cm} is negligible. However, it does not seem profitable to try to extract meaningful information from this slight changes.

Crystallization kinetics of PVDF previously reported by Mancarella and Martuscelli²⁰ reports considerably different values of n and K with our results. But the half-time $t_{1/2}$ in their report is much longer than our results and it is assumed that their samples have comparatively high molecular weight. Therefore, direct comparison between two data is meaningless.

3-2. Non-isothermal Crystallization

The kinetics of non-isothermal crystallization can be characterized by the application of two procedures²¹. The former is based on the accep-

tance of the simplifying assumption that crystallization occurs under constant temperature. The latter procedure is based on the approximate theory formulated by Ziabicki²² which is based on the assumption that crystallization can be presented by means of the relationship for the first order kinetics.

In this study we have approached via the latter procedure. In this case the rate constant $K(T)$, which is dependent only on temperature, can be described by the following empirical equation:

$$K(T) = K_{\max} \exp[-4(\ln 2)(T - T_{\max})^2/D^2] \quad (5)$$

where K_{\max} is the maximum value of the rate constant corresponding to the temperature T_{\max} ; D , defined as $T_{D1} - T_{D2}$, is the half width of the crystallization curve (Fig. 11).

Crystallization of polymers is limited to the range between glass transition and melting temperature. Hence, we can calculate the quantity G , known as 'the kinetic crystallizability':

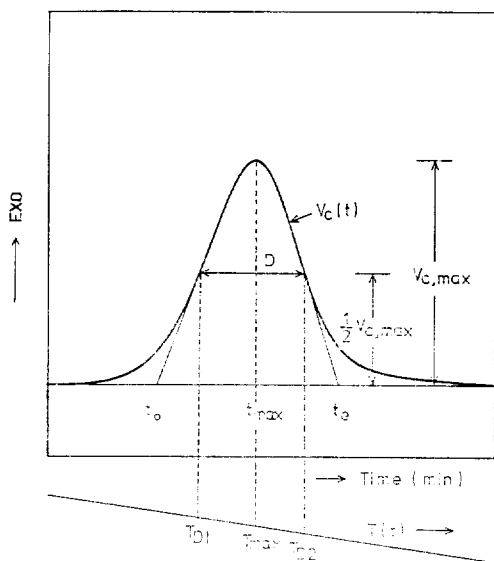


Fig. 11. Typical D.S.C. thermogram of nonisothermal crystallization of the polymer sample. Weight fraction of PMMA, 5%; cooling rate, $dT/dt = -5^\circ\text{C}/\text{min}$.

$$G = \int_{T_f}^{T_m} K(T) dT = (\pi/\ln 2) K_{\max} D/2 \quad (6)$$

This parameter requires proper correction, considering the cooling rate of the polymer. The final form will be as follows:

$$G_c = G/(dT/dt) \quad (7)$$

where dT/dt is the cooling rate. G_c parameter can be successfully used for characterizing the kinetics of non-isothermal crystallization since this parameter is not dependent on the conditions of the crystallization process, and particularly on the cooling rate.

The K_{\max} value, corresponding to temperature T_{\max} , in which the crystallization rate is maximum, should now be calculated as follows²¹:

$$K_{\max} = C_K (t_{\max})^{-1} \quad (8)$$

where

$$C_K = \int_{t_0}^{t_{\max}} V_c(t) dt / \int_{t_{\max}}^{t_e} V_c(t) dt \quad (9)$$

The results of the determination of parameters characterizing the non isothermal crystallization of the blends under the cooling rate of $-5^\circ\text{C}/\text{min}$ are given in Table 4.

As can be seen in Table 4, the values of G_c decreases considerably with PMMA concentration. It means that the amorphous PMMA has an unfavorable effect on the non-isothermal crystallization process of PVDF in blends. These results are in accord with the isothermal case. Hence, we can conclude that the crystallization rate decreases markedly with PMMA content in both isothermal and non-isothermal crystallization process.

Table 4. Parameters Characterizing Non-Isothermal Crystallization Kinetics of the Blend

conc. of PMMA (%)	t_{\max} (min)	C_K	K_{\max} (min^{-1})	D ($^\circ\text{C}$)	G ($^\circ\text{C}/\text{min}$)	G_c
0	0.570	1.273	2.233	2.95	7.012	1.402
5	0.530	1.202	2.072	3.10	6.837	1.367
10	0.680	1.232	1.812	3.50	6.751	1.350
15	0.925	0.972	1.051	5.25	5.873	1.175

4. CONCLUSIONS

The melting point depression and changes in melt crystallization temperature are the supporting evidences of the miscibility of PVDF-PMMA blend.

The overall rate of crystallization ascertained by DSC is strongly affected by the presence of PMMA. The kinetic rate constant K decreases markedly with PMMA concentration. It may be explained that the increase in T_g and the decrease in T_m , i.e., decrease in the gap ($T_m - T_g$), will retard molecular motion and then restrict crystallization.

The Avrami exponent n decreases slightly with increasing PMMA content. Hence, it can be presumably assumed that the growth dimension becomes lower as the addition of PMMA.

In the non-isothermal crystallization kinetics, the kinetic crystallizability G decreases considerably with the PMMA concentration. Therefore, it can be concluded that the crystallization rate decreases considerably with PMMA content in both isothermal and non-isothermal process.

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