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Poly (ethylene terephthalate) 와 Polycarbonate 블렌드의 비등온 결정화 속도에 관한 연구

조 원 호 · 김 성 동

서울대학교 공과대학 섬유공학과

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The Non-Isothermal Crystallization Kinetics of Poly (ethylene terephthalate) and Polycarbonate Blend

Won Ho Jo and Sung Dong Kim

Department of Textile Engineering, Seoul National University
Seoul, 151, Korea

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Abstract: The non-isothermal crystallization kinetics of poly(ethylene terephthalate) from the blends of poly(ethylene terephthalate) and bisphenol. A polycarbonate were studied at various cooling (or heating) rates. The non-isothermal crystallizations were measured with differential scanning calorimetry. Ziabicki's approximate theory, Avrami equation and Jeziorny's and analysis of thermogram were employed to analyze the non-isothermal crystallization behavior. It was found that the addition of polycarbonate retarded the crystallization rate considerably and decreased the crystallinity. Rapid cooling (or heating) increased the crystallization rate due to athermal nucleation, but at the cooling (or heating) rate of 30°C/min the crystallinity of blends tended to decrease. Avrami exponent n for non-isothermally crystallized samples was found to be in the range of 2.2-2.3.

1. INTRODUCTION

The observation of crystallization may provide a useful way to obtain fundamental information about polymer blend. First, if the two polymers are compatible, the diffusion of the non-crystallizable polymer plays a very important role in the crystallization and causes melting point depression which is the result of lowering the chemical potential of crystallizable polymer. Second, blending may offer a good method to control the rate of crystallization and subsequently the level of crystallinity developed under particular processing conditions.

The kinetics of isothermal process has been thoroughly studied by using Avrami equation[1-6]. But in practical processes including melt spinning of synthetic fibers and fabrication of crystalline

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*This paper is devoted to Professor Jyong Sup Shim for honoring his 60th birthday.

polymers crystallization occurs under non-isothermal condition. Nevertheless few attempts to elucidate the kinetics of dynamic, non-isothermal process have been made.

Ziabicki[7] proposed the kinetic crystallizability which was evaluated by the reciprocal of experimentally observed crystallization half time. According to the theory, the kinetic crystallizability characterizes the degree of crystallinity obtained when material was cooled at a constant cooling rate from the melting temperature to the glass transition temperature. Ozawa[8] extended the Avrami equation to the non-isothermal situation, assuming that amorphous polymer was cooled at a constant rate. He found that the nuclei of crystallization of poly(ethylene terephthalate) were randomly formed during crystallization and that the crystallites grew three dimensionally. Nakamura et al.[9] analysed non-isothermal crystallization in terms of data of isothermal crystallization. They derived an equation which described the degree of phase transformation on the assumption of the isokinetic conditions. Jeziorny[10] proposed the method of determining the parameters characterizing the kinetics of non-isothermal crystallization on the basis of differential scanning calorimetry thermograms. Considering the different cooling rate, he modified Ziabicki's theory into an easily applicable form.

In recent years much efforts have been devoted to studying the crystallization and the resulting morphology of binary compatible systems, in which one or both of the components are crystallizable. The blend of poly(ethylene terephthalate) with bisphenol-A polycarbonate is one of these systems and has been the object of various patents and study[11]. The main object of this paper is to examine the effect of polycarbonate on the non-isothermal crystallization rate of the blends and the crystallization behaviors at different cooling (or heating) rates.

2. EXPERIMENTAL

2-1. Preparation of samples

Bisphenol-A polycarbonate (PC) used in this study was Panlite L-1250 manufactured by Teijin Chemicals Ltd. Poly(ethylene terephthalate) (PET) ($\overline{M}n = 20,000$) was provided by Tong Yang Nylon Co., Ltd.

Pellets of the two polymers were dry blended to the desired compositions and kept in a vacuum oven at 125°C overnight. Blends were prepared by melt mixing in a Brabender Plasticorder model PLE 330 at 280°C followed by quenching in cold water.

2-2. Thermal analysis

Thermal analyses were performed by Du Pont 1090 Thermal Analyzer with a Differential Scanning Calorimetry (DSC) 910 module under nitrogen gas purging. The temperature calibration was done by use of Indium metal.

The thermal programs for DSC analysis are illustrated in Fig. 1. Program (a) was for examining the non-isothermal crystallization at various cooling rates. In this program the samples were heated to 270°C with a rate of 50°C/min, maintained for 10 min isothermally to ensure complete melting of the PET crystals and then cooled with rates of -30°C/min, -20°C/min, and -10°C/min to room

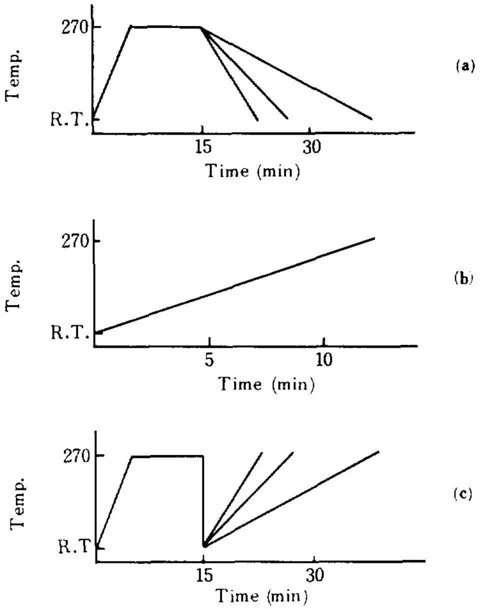

Fig. 1. Thermal programs used for differential scanning calorimetry.

temperature. Program (b) was for studying the melting behaviors of the samples crystallized by program (a). In this program the samples were heated from room temperature to 270°C with a rate of 20°C/min. Program (c) was for obtaining thermograms of cold crystallization at different heating rates. In this program each sample was melted completely at 270°C for 10 min and quenched to room temperature to yield amorphous state and heated to 270°C with rates of 30°C/min, 20°C/min, and 10°C/min.

3. THEORY

The kinetics of non-isothermal crystallization has been quantitatively analyzed by the use of Ziabicki's approximate theory[7,12] and Jeziorny's approach[10]. These theories are based on the assumption that crystallization can be represented by means of the equation for first order kinetics:

$$\frac{dX_t}{dt} = K(T)\,[1 - X_t] \tag{1}$$

where, K(T), the rate constant is dependent only on temperature and X_t is the degree of crystallinity after time t of the crystallization process.

K(T) can be expressed by the following empirical equation:

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

where, K_{max} is the maximum value of the rate constant corresponding to the temperature T_{max} and D is the half width of the K(T) curve.

The kinetic crystallizability (G) represents the resulting degree of crystallinity obtained over the entire crystallization range and can be calculated as follow:

$$G = \int_{Tg}^{Tm} K(T)\,dT = (\pi/\ln 2)^{\frac{1}{2}} K_{max} D/2 \tag{3}$$

Considering the cooling rate of the polymer, Jeziorny proposed the corrected kinetic crystallizability (G_c) which is not dependent on cooling rate.

$$G_c = G/(dT/dt) \tag{4}$$

where, dT/dt is the cooling rate.

In order to obtain G and K_{max} from DSC ther-

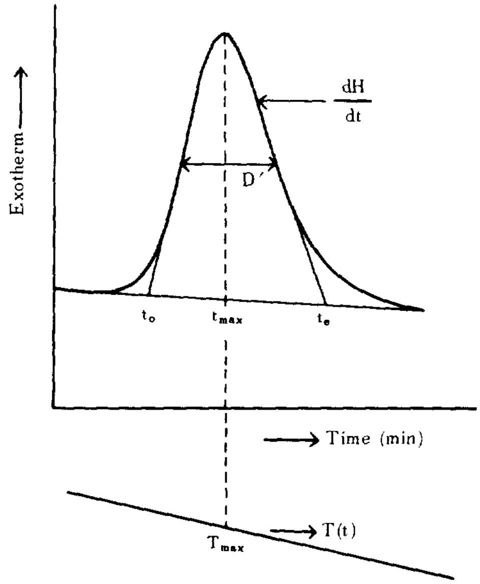

Fig. 2. Typical D.S.C. thermogram of non-isothermally crystallized PET at a cooling rate of 20°C/min.

tion of enthalpy of crystallization and D' is the half width of thermogram.

On integration of eq. 1 from the starting time (t_o) to the final time of crystallization (t_e) we obtain

$$-\ln(1 - X_e) \simeq \int_{t_o}^{t_e} K(T)\,dt \tag{5}$$

where, X_e is the final degree of crystallinity. The heat of fusion of fully crystalline PET is 28.1 cal/g[13], then X_e is expressed as eq. 6.

$$X_e \simeq \frac{\int_{t_e}^{t_o}(dH/dt)\,dt}{28.1} = \frac{\Delta H_c}{28.1} \tag{6}$$

where, ΔH_c is the heat of crystallization.

Introducing the ratio of crystallinity (C_k) before and after t_{max},

$$C_K = \int_{t_o}^{t_{max}} K(T)\,dT / \left[\int_{t_e}^{t_e} K(T)\,dT - \int_{t_o}^{t_{max}} K(T)\,dT\right]$$

one obtain eq. 7:

$\int^{t_{max}} K(T)\,dt = C_K$ [illegible] $\int^{t_e} K(T)\,dt$ (7)

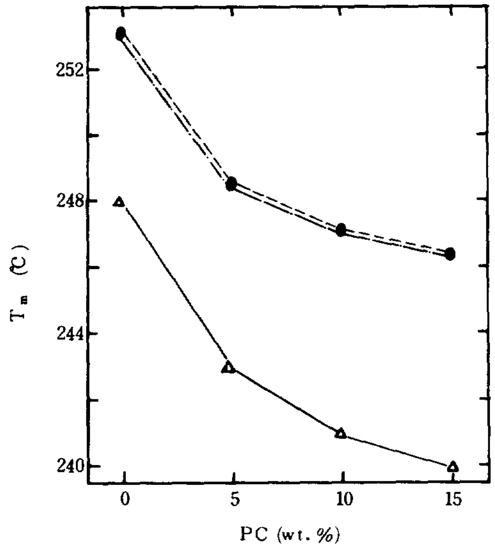

Fig. 6. Plots of the melting temperature vs. concentration of PC at various cooling rates: ○, -30°C/min; ●, -20°C/min; △, -10°C/min.

tration because the increase in PC content causes the increase of amorphous fraction in the blend. If PC has no effect on the crystallization of PET, ΔH_c° must be constant. But ΔH_c° exhibits a tendency of decreasing in Fig. 5.

In Fig. 6, there is a trend for melting temperature to decrease. This depression is mainly due to the result of lowering the chemical potential of PET by the addition of PC[16]. The melting point depression is the evidence that the two polymers are miscible each other.

The values of parameters determined by the use of eqs. 3,4 and 9 are shown in Table 1 and plotted in Figs. 7-9. K_{max}, G, and G_c tend to decrease as the PC concentration increases. The reason may be explained as follows: for polymer blends where the crystallization of one polymer takes place in the presence of a noncrystallizable one, the diffusion of crystallizable polymer segments to the crystallite liquid interface becomes very important[17]. The addition of miscible polymer to a crystallizable polymer will lower the crystallization rate if the T_g of blend is higher than that of the crystallizable polymer, which means molecular motion is restricted. On the other hand, a higher crystallization rate will be expected if the T_g of blend is lower than that of the crystallizable polymer. The T_g of the blends are

Table 1. Parameters Characterizing the Non-Isothermal Crystallization Kinetics of the Blends at Different Cooling Rates

cooling rate (°C/min)	conc. of PC (wt.%)	D′ (min)	t_{max} (min)	C_k	K_{max} (min^{-1})	G (°C/min)	G_c
-30	0	0.43	0.32	0.78	1.10	14.18	0.47
	5	0.62	0.48	0.79	0.57	10.61	0.35
	10	0.85	0.68	0.85	0.33	8.47	0.28
	15	0.93	0.70	0.97	0.26	7.23	0.24
-20	0	0.54	0.41	0.75	0.86	9.33	0.47
	5	0.75	0.60	0.86	0.51	7.67	0.38
	10	1.05	0.85	0.85	0.33	6.84	0.34
	15	1.10	0.88	0.76	0.27	5.95	0.30
-10	0	0.83	0.63	0.78	0.57	4.68	0.47
	5	1.30	1.05	0.85	0.30	3.93	0.39
	10	1.50	1.25	0.87	0.30	3.93	0.39
	15	1.50	1.30	0.96	0.20	2.96	0.30

higher than that of pure PET, as shown in Table 3. The same trend was reported in previous paper[11]. Therefore, the diffusion of crystallizable polymer to the growth sites become difficult and the crystallization rate and crystallinity of the blends decrease.

Fig. 7 shows that K_{max} increases with the cooling rate. This is due to athermal nucleation[12,18]. The nucleation rate consists of two different contributions. The first one is related to thermal fluctuations leading to the formation of molecular clusters of super critical size. The other, atermal, appears only when the thermodynamic state of system is changed. The athermal nucleation rate is proportional to the rate with which the system changes its state, i.e., it is propertional to the cooling (or heating) rates, etc. Therefore, the athermal nucleation and greater driving force caused by larger supercooling make the crystallization rate increase. The increase in K_{max} at the change of the cooling rate from -20°C/min to -30°C/min is smaller than that at the change of the cooling rate from -10°C/min to -20°C/min. This is due to the decrease in heat of crystallization which plays an important role in calculating the K_{max} (eq. 9).

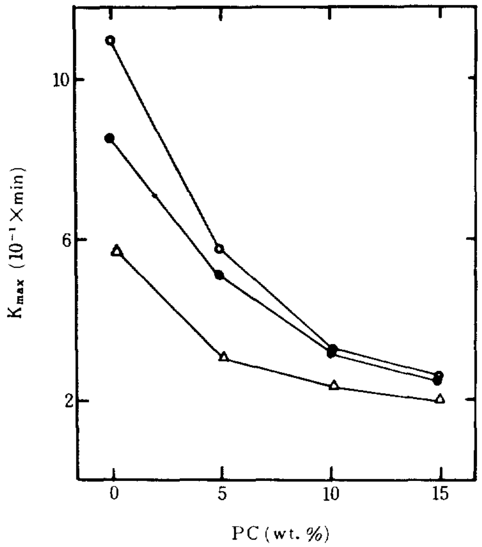

Fig. 7. Plots of maxmum crystallization rate vs. concentration of PC at various cooling rates: ○, -30°C/min, ●, -20°C/min; △, -10°C/min.

The non-isothermal crystallization thermogram was also analyzed by means of the Avrami equation[19]. It is found from Avrami plots that the Avrami exponent of non-isothermally crystallized samples is in the range of 2.2-2.3.

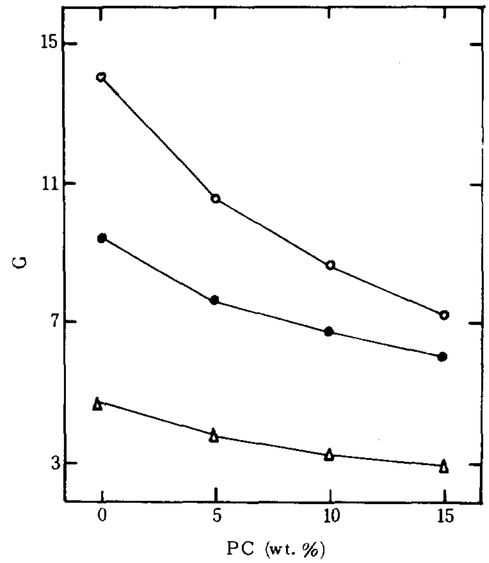

Fig. 8. Plots of the kinetic crystallizability vs. concentration of PC at various cooling rates: ○ -30°C/min; ●, -20°C/min; △, -10°C/min.

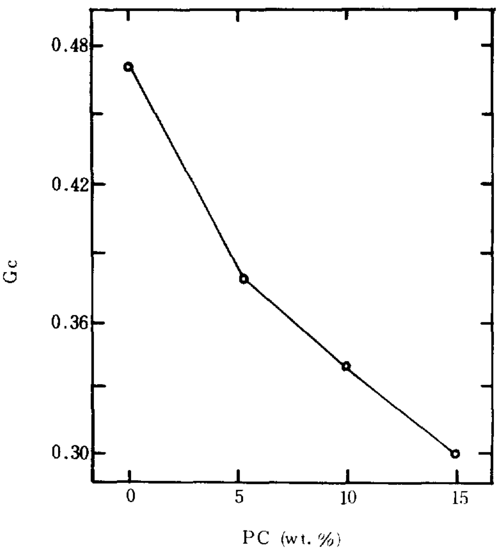

Fig. 9. Plots of the corrected kinetic crystallizability vs. concentration of PC.

Wunderlich[2] reported that the overall crystallization kinetics of iso-thermally crystallized PET changed from Avrami exponent n = 2 at 90-160°C to n = 3 at 180-230°C, to finally n = 4 above 230°C. The discrepancy between the value of n obtained isothermally seems to be caused by athermal nucleation.[12] As shown in Table 2, K decreases with the addition of PC and the reciprocal of crystallization half-time ($t_{1/2}^{-1}$), which is taken as a measure of overall rate of crystallization, also decreases. This result coincides with the kinetic crystallizability.

Table 2. Avrami Exponent (n) and Crystallization Half-Time ($t_{1/2}$) and Kinetic Rate Constant (K) of Non-Isothermally Crystallized Samples

cooling rate (°C/min)	conc. of PC (wt.%)	n	$t_{1/2}$ (min)	k (min^{-n})
-30	0	2.29	0.35	7.54
	5	2.32	0.52	3.22
	10	2.33	0.74	1.42
	15	2.30	0.76	1.32
-20	0	2.29	0.45	4.37
	5	2.26	0.63	1.99
	10	2.29	0.87	0.95
	15	2.28	0.94	0.80
-10	0	2.26	0.68	1.69
	5	2.25	1.10	0.60
	10	2.31	1.28	0.39
	15	2.27	1.34	0.36

In order to examine crystallization behavior from glassy state, cold crystallization was performed at different heating rates. All data are shown in Table 3. The rate of crystallization shows the same tendency as the melt crystallization. In cold crystallization, T_c increases with PC content, which also indicates qualitatively that the crystallization of the blend is retarded.

5. CONCLUSIONS

The melting point depression and changes in crystallization temperature are the evidence of the miscibility of poly(ethylene terephthalate) and polycarbonate.

The addition of polycarbonate retards the

Table 3. Parameters Characterizing the Non-Isothermal Crystallization Kinetics of the Blend at Different Heating Rates

heating rate (°C/min)	conc. of PC (wt.%)	K_{max} (min^{-1})	G (°C/min)	G_c	T_g (°C)	T_c (°C)	T_m (°C)
30	0	1.38	13.32	0.45	80.0	147.0	253.0
	5	0.63	10.75	0.36	82.0	165.0	247.5
	10	0.40	9.11	0.30	83.0	177.5	247.0
	15	0.28	7.56	0.25	85.0	183.0	245.5
20	0	0.90	9.03	0.45	79.0	141.5	253.0
	5	0.50	7.26	0.36	81.0	159.0	248.0
	10	0.36	6.73	0.34	82.0	167.5	247.0
	15	0.27	5.44	0.27	83.5	171.5	246.5
10	0	0.49	4.18	0.42	77.5	134.5	254.5
	5	0.30	3.50	0.35	79.0	149.5	249.0
	10	0.25	3.32	0.33	82.0	156.5	248.5
	15	0.22	3.03	0.30	82.5	161.0	248.0

molecular motion and thus restricts strongly the rate of crystallization of the blend. It is supported by the fact that both kinetic crystallizability and kinetic rate constant decrease as the polycarbonate concentration increases.

Since non-isothermal crystallization causes athermal nucleation, the rapid cooling (or heating) increases the crystallization rate. But at the cooling (or heating) rate of 30°C/min the crystallinity of the blend tends to decrease.

Avrami exponent n for non-isothermally crystallized samples is in the range of 2.2-2.3.

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