

An Efficient Organic Additive to Control the Crystallization Rate of Aliphatic Polyketone: A Non-isothermal Crystallization Kinetics Study

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Abstract Three types of organic compounds—two carboxylic acids and an anhydride, were used as additives for polyketone (PK). The effect of the additive structure and their feed ratios on the melting temperature, crystallization temperature, and crystallization rate of PK were studied. We found that the crystallization temperature could be reduced significantly by introducing a small quantity of organic additive, in particular, an anhydride. On addition of 1 phr of anhydride, the crystallization temperature was reduced by 10.7 °C. Therefore, the non-isothermal crystallization kinetics of aliphatic PK/anhydride blends with various feed ratios was investigated using DSC. The results were analyzed by various theoretical models, such as Avrami, Ozawa and combined Avrami-Ozawa models.

Keywords Polyketone; Anhydride; Non-isothermal; Crystallization kinetics

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INTRODUCTION

Aliphatic polyketones (PK) are a group of engineering plastics with a unique combination of good thermal, mechanical, barrier, and chemical resistance properties. This property set is similar to that of polyamides and polyacetals^[1]. These properties give PK significant commercial potential in a broad range of engineering, barrier packaging, fiber, and blending applications. However, PK is characterized as a highly crystalline material with a melting point of ~250 °C, and the high melting temperature (T_m) has limited the applications of this copolymer because degradation occurs rapidly at processing temperatures (approximately 25 °C above T_m)^[2].

So far, the most successful method to improve the processability of PK has been to incorporate propylene, thus producing a polyketone terpolymer of ethylene, propylene, and carbon monoxide. The T_m of the product polymer can be lowered by incorporating propylene monomers into the polymer chain, which reduces the chain regularity of the terpolymers. By introducing the propylene monomer, the T_m s of the polyketone terpolymer can be controlled in the range of 220–230 °C^[3–5]. These terpolymers display a balance of toughness, stiffness, chemical resistance, and ease of processing, which makes them suitable for several applications (such as in appliance, automotive, and electrical industries)^[2]. The decrease in T_m means that the polyketone can be processed at lower temperatures without significant product degradation^[6]. However, although the introduction of comonomer results in a ~25 °C reduction in T_m , a major unresolved problem is the fast crystallization rate,

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which limits commercial utilization especially as an engineering plastic.

Therefore, we sought to find an efficient organic additive that could be used to control both the temperature and rate of crystallization of aliphatic PK. The effects of the additive structures and feed ratios on the thermal properties, isothermal, and non-isothermal crystallization kinetics of aliphatic PK were investigated using DSC and XRD. The experimental data were analyzed based on various theoretical models, such as Avrami, Ozawa, and combined Avrami-Ozawa models. Additionally, by using the Kissinger and Takhor model, the activation energy of crystallization was calculated.

EXPERIMENTAL

Materials and Preparation of Compounds

The aliphatic polyketone (PK, C₃: 2.7 mol%, MI = 20 g/10min at 240 °C, 2.16 kg) was supplied by Hyosung Co., Korea. 3,3',4,4'-Benzophenonetetracarboxylicdianhydride (BTDA, Alfa Aesar, England), citric acid (CA, Duksan Chemical Co., Korea), and poly(acrylic acid) (PAA, $M_w = 4.5 \times 10^5$, Sigma Aldrich, US) were used without further purification.

Dried polyketone and various additives were melt mixed using a twin-screw mixer (Plasticoder Brabender, PLE331). The compounds were mixed at 100 r/min for 5 min at 230 °C.

DSC Measurements

A differential scanning calorimeter (DSC, Setaram DSC131 evo) was used to measure the melting and crystallization behavior at constant heating or cooling rates. In addition, DSC was used to analyze the isothermal and non-isothermal crystallization behaviors of the pure aliphatic PK and PK/additive mixtures. To prevent thermal oxidative degradation of the materials, all measurements were performed under a nitrogen atmosphere. To avoid uneven thermal conduction, the samples were maintained at a constant weight of (7 ± 1) mg. For melting and crystallization of the PK, the samples were heated from room temperature to 240 °C at a scanning speed of 20 K/min and held at that temperature for 2 min to remove prior deformation and thermal history. Then, the sample was cooled rapidly in liquid nitrogen. Following this treatment, the sample was reheated to 240 °C at a scanning speed of 10 K/min and cooled at the same scanning speed.

For non-isothermal crystallization, the samples were heated from room temperature to 240 °C at a rate of 30 K/min, and held at that temperature for 2 min. Then, they were cooled at several different rates, *e.g.*, 2, 5, 10, 20 and 40 K/min. The exothermic crystallization peaks were recorded as a function of temperature.

X-ray Diffraction Analysis

Wide-angle X-ray scattering diffractometer (WAXD) patterns were obtained in reflection mode using a Rigaku D/Max-2500 diffractometer and Cu K α radiation. Film samples were prepared (10 mm $\times$ 10 mm) with thickness of approximately 1.0 mm. The samples were annealed in a vacuum oven at 100 °C.

RESULTS AND DISCUSSION

Effect of Additives on Melting and Crystallization Temperature

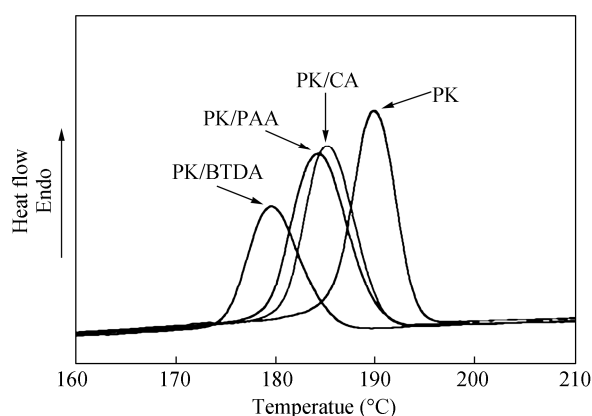
Firstly, the melting crystallization properties of PK and PK/additives were measured by DSC. The DSC curves and T_m results are given in Fig. S1 (in supporting information, SI) and Table 1, respectively. We found that introduction of additives led to a significant reduction in the T_m of PK. This reduction may be related to a significant reduction in crystallite size in the presence of additives. On addition of 1 part per hundred resin (phr) of additive, the T_m of PK was reduced by 9.0, 3.8 and 2.9 °C for BTDA, CA, and PAA, respectively. Additionally, the T_m of PK decreased almost linearly with increasing additive feed ratio. The effect of each addition per unit weight on the efficiency was found to decrease in the following order: BTDA > CA > PAA. Importantly, the decrease in T_m means that the PK/additives could be processed at relatively low processing temperatures, which in turn reduced product degradation during processing.

The effect of additives on the crystallization temperature (T_c) of PK was also studied. As shown in Table 1 and Figs. 1 and S2 (in SI), the T_c of PK was dramatically affected by the structure and quantity of the additives.

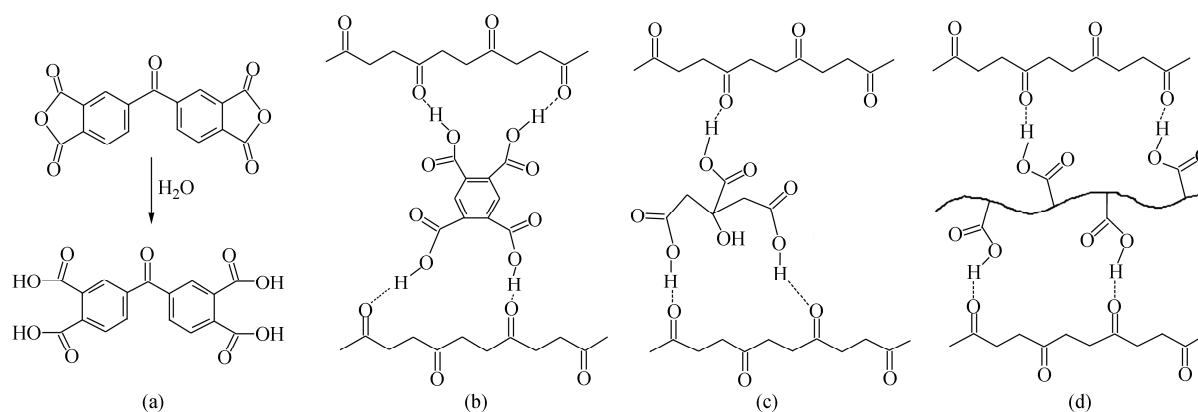
For BTDA, the T_c of PK decreased to 184.0 and 176.3 °C for addition of 0.5 phr and 1.5 phr, respectively; the T_c of PK is 190.3 °C. The crystallization rate can be calculated by measuring the width at half height (FWHM) of the crystallization exotherm. Interestingly, the FWHM values of the crystallization exotherms significantly increased on introduction of organic additives. These results suggest a decrease in crystallization kinetics on adding the additive. BTDA has a greater effect on T_c than PAA, but similar FWHM values of the crystallization exotherms were observed for both additives.

Table 1 Thermal properties of PK and PK/additives

Polymer	Content (phr)	T_m (°C)	T_c			
			Max (°C)	Onset (°C)	Offset (°C)	Onset – Offset (°C)
PK		224.5	190.3	194.3	186.4	7.9
PK/BTDA	0.5	219.5	184.0	189.2	179.8	9.5
	1.0	215.5	179.6	185.1	175.0	10.1
	1.5	211.8	176.3	181.5	171.7	9.8
PK/CA	0.5	222.0	187.7	192.3	183.9	8.4
	1.0	220.7	185.1	190.3	180.9	9.4
	1.5	218.5	184.1	189.1	180.1	9.0
	2.0	218.5	183.2	188.4	179.1	9.4
PK/PAA	0.5	221.1	186.2	191.0	182.4	8.6
	1.0	221.6	184.2	189.5	179.3	10.1
	1.5	219.3	182.8	188.2	178.4	9.9
	2.0	219.2	182.4	188.1	177.8	10.3
	5.0	215.9	175.7	183.6	171.1	12.5

**Fig. 1** Melt crystallization thermograms of PK, PK/CA, PK/PAA and PK/BTDA (additive content: 1.0 phr)

The proposed interaction mechanisms between PK and the additives are shown in Scheme 1. Concerning that of BTDA, BTDA is hydrolyzed *in situ* by physically absorbed water (Scheme 1a) gained during processing, and the resulting carboxylic acid groups can form hydrogen bonds with the PK matrix (Scheme 1b)^[7, 8]. For CA and PAA additives, the carboxylic acid groups are directly hydrogen bonded to the PK matrix, forming a pseudo-crosslinked structure (Schemes 1c and 1d). Therefore, the interaction between PK and additives lead to drastically reduced values of T_m and T_c due to the disruption of the regular structure of PK.



Scheme 1 Proposed interaction mechanism of PK and additives (a, b: BTDA, c: CA and d: PAA)

As shown in Fig. S1 (in SI), doublet melting peaks are observed for both PK and PK/additives. No evidence of an endotherm associated with an α - β transition was observed, and this is because the specimen was prepared at 230 °C, a sufficiently high temperature to ensure transformation of the α phase to the β phase. Notably, the PK α phase cannot be re-formed on cooling, indicating the irreversibility of the transition^[9, 10]. Therefore, the doublet melting peaks reflect the melting behavior of β -phase crystals only. In addition, other researchers^[9] have reported the sole presence of the β phase of PK after crystallization with propylene content greater than 5 mol%.

To confirm the phase structure and degree of crystallinity in detail, WAXD analysis of PK and PK/additives was carried out, and the results are given in Fig. 2. According to the literature, PK chains crystallize in two different phases: α and β . As shown in Fig. 2, only peaks due to the β phase of PK were observed in WAXD patterns. The WAXD patterns of PK and PK/additives showed diffraction peaks at $2\theta = 21.6^\circ$, 24.6° , 28.7° , 37.9° , and 39.6° , corresponding to the 110/200, 201, 210, 310, and 120 Miller planes of PK, respectively, suggesting the presence of the crystalline β phase of PK^[9, 10]. In addition, all specimens showed the same main diffraction peaks at the same locations, indicating that the samples had the same crystal structure despite their different T_c s. This result suggests that only the β phase is expected for the present terpolymers after crystallization, even after the addition of additives. Therefore, we concluded that the presence of the propylene units destabilized the α phase with respect to the β phase, in agreement with the conclusion of Klops *et al.*^[9].

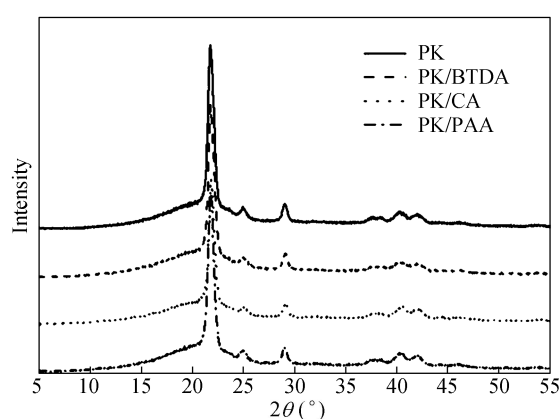


Fig. 2 WAXD patterns of PK and PK/additives (additive content: 1.5 phr)

X-ray diffraction is the primary method used to determine the degree of crystallinity (X_c). Values of X_c of PK and PK/additives were calculated from the X-ray patterns, and these values are slightly higher than DSC

measurements. The X_c values calculated from XRD are 32%, 28%, 30% and 32%, for PK and PK with 1.5 phr BTDA, CA, or PAA addition, respectively. It was found that the crystallinity of PK reduced with the addition of BTDA. This phenomenon was further confirmed by DSC. For DSC calculation, assuming the heat of fusion for 100% crystalline terpolymer is equal to that of the copolymer, 227 J/g^[10]. The X_c values of neat PK and PK with 1.5 phr BTDA, CA or PAA addition are 29%, 25%, 27% and 31%, respectively. Although these additives did not affect the phase structure of PK, the X_c of PK slightly decreased with the addition of BTDA. We considered that BTDA interrupted the crystallization of PK due to the interactions between the anhydride moiety of BTDA and carbonyl groups of aliphatic PK. Therefore, BTDA is the most efficient additive to reduce the crystallization rate of PK.

Non-isothermal Crystallization Behavior

Because most processing techniques occur under non-isothermal conditions, an understanding of non-isothermal crystallization behavior is of practical importance. Furthermore, studies related to the kinetics of crystallization are key to understanding the relationship between processing conditions and the properties of the end products^[11, 12].

The crystallization exotherms of PK, PK/BTDA, PK/CA, and PK/PAA at various cooling rates are shown in Fig. S3 (in SI), and the exothermal parameters are summarized in Table S1 (in SI). The maximum crystallization peak (T_p) and crystallization onset peak (T_0) shifted to lower temperatures on increasing the cooling rate. This can be explained as follows: the chains of PK have sufficient time to pack up in a unit cell at lower cooling rates, and then, PK nuclei grow at higher temperature. In contrast, at faster cooling rates, the chains of PK do not have enough time to become arranged regularly or to form crystal nuclei. Thus, crystallization occurs at lower temperature^[13].

Although all the additives inhibited crystallization of pristine PK, the decrease observed for PK/BTDA was greater than that of the other additives. Therefore, we systematically studied the non-isothermal kinetics of PK/BTDA in comparison with that of pristine PK.

Figure 3 shows the plots of the relative degree of crystallinity ($X(t)$) as a function of time for PK and PK/BTDA non-isothermally crystallized at five different cooling rates (ϕ). The time taken to complete crystallization was reduced with increasing cooling rate, while the relative crystallinity of PK/additives was lower than that of pristine PK after the same time for complete crystallization. These results suggest that the incorporation of additives reduces the overall crystallization process. In addition, a parameter that can be directly obtained from the degree of crystallinity as a function of time is the half-time of crystallization, $t_{1/2}$. This value is the change in time from the onset of crystallization to the time at 50% completion. We found that the value of $t_{1/2}$ became significantly lower at faster cooling rate. By comparing these values with those of pristine PK, the $t_{1/2}$ values of PK/BTDA are somewhat higher at the same cooling rate (Table 2), reflecting that the addition of BTDA inhibits nucleation and consequently reduces the crystallization rate of PK.

In the Avrami model^[14–17], the time dependent crystallization is modeled as Eqs. (1) and (2):

$$1 - X(t) = \exp(-G_t t^n) \quad \text{or} \quad \lg[-\ln(1 - X(t))] = n \lg t + \lg G_t \quad (1)$$

$$\lg G_c = \lg G_t / \phi \quad (2)$$

where G_c and G_t are growth parameters, and n is the Avrami exponent.

Figure 4 shows double logarithmic plots of $\lg[-(1 - X(t))]$ versus $\lg t$ for PK and PK/BTDA samples cooled at various rates. The plots are not linear over the entire range of crystallization time, indicating that the modified Avrami equation does not perfectly describe the non-isothermal crystallization of PK or PK/additive samples. Each curve has a linear portion, which is followed by a slight deviation after longer time periods. Usually, this deviation is considered to be due to secondary crystallization, which is caused by spherulite impingement during the later stages of crystallization. However, the adjusted r^2 values of all plots were > 0.99 , suggesting that the Avrami method can be used to investigate non-isothermal crystallization kinetics of PK and PK/BTDA

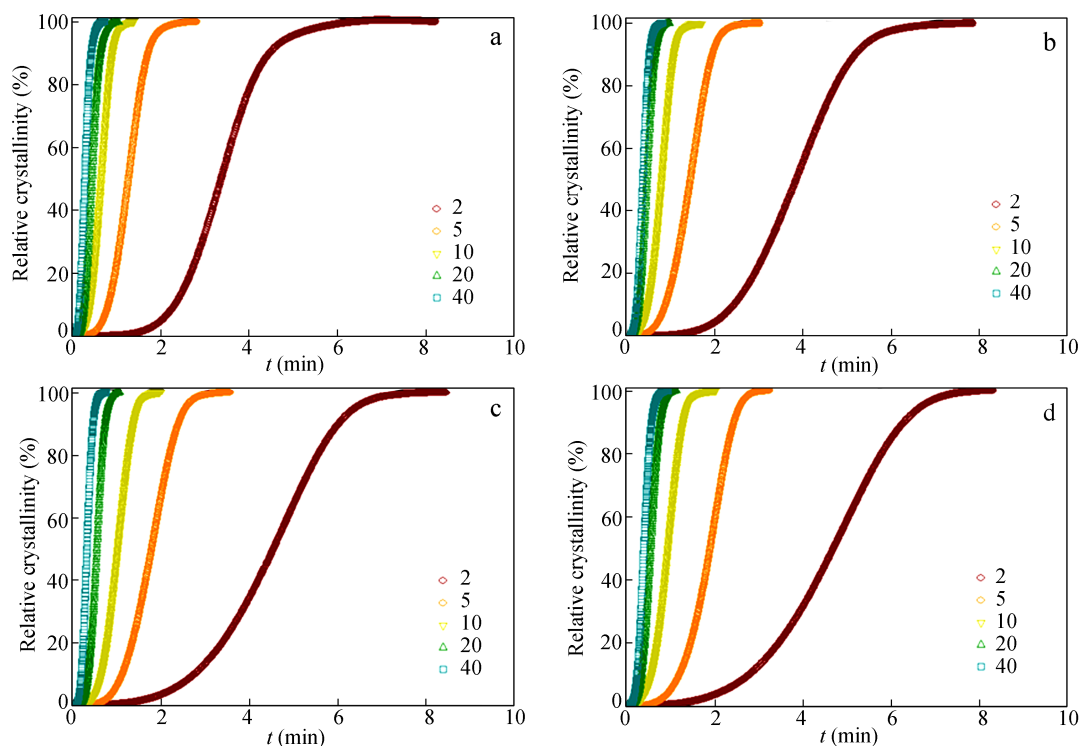


Fig. 3 Plots of relative crystallinity as a function of time at various cooling rates of (a) PK and PK with different BTDA contents: (b) 0.5 phr, (c) 1.0 phr and (d) 1.5 phr

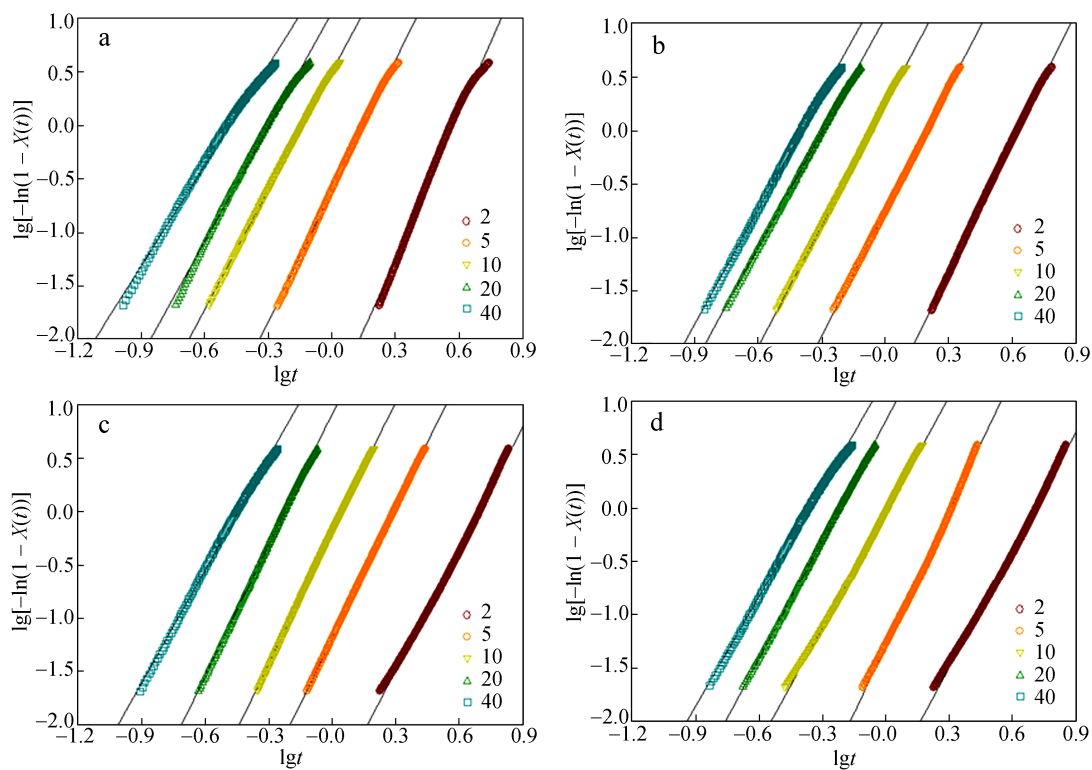


Fig. 4 Plots of $\lg[-\ln(1 - X(t))]$ versus $\lg t$ for (a) PK and PK with different BTDA contents: (b) 0.5 phr, (c) 1.0 phr and (d) 1.5 phr

compounds. As shown in Fig. 4, the linear portions are almost parallel to each other, shifting to shorter time at more rapid cooling rates. This indicates that the nucleation mechanism and crystal growth geometries are similar for both primary and secondary crystallization at all cooling rates. The values of the Avrami exponent (n), the crystallization half-time ($t_{1/2}$), and the rate parameter (G_t), determined from the slopes and intercepts of the selected plots, are shown in Table 2.

Table 2 Non-isothermal crystallization kinetic parameters from modified Avrami equation for PK and PK/BTDA at various cooling rates

	ϕ (K/min)	$t_{1/2}$ (min)	n	$\lg G_t$	G_c	r^2
PK	2	3.374	4.52	-2.61	0.050	0.991
	5	1.277	4.10	-0.62	0.752	0.998
	10	0.656	3.73	0.51	1.125	0.999
	20	0.444	3.58	1.06	1.130	0.995
	40	0.283	3.14	1.51	1.091	0.994
PK/BTDA (0.5 phr)	2	3.847	4.06	-2.55	0.053	0.999
	5	1.445	3.86	-0.76	0.705	0.999
	10	0.786	3.77	0.24	1.057	0.999
	20	0.455	3.59	1.06	1.130	0.999
	40	0.360	3.57	1.40	1.084	0.998
PK/BTDA (1.0 phr)	2	4.545	3.81	-2.64	0.048	0.998
	5	1.785	4.09	-1.19	0.578	0.999
	10	1.015	4.13	-0.20	0.955	0.999
	20	0.542	4.13	0.93	1.113	0.999
	40	0.315	3.53	1.57	1.095	0.998
PK/BTDA (1.5 phr)	2	4.694	3.67	-2.60	0.050	0.998
	5	1.894	4.22	-1.30	0.550	0.997
	10	0.932	3.62	-0.04	0.991	0.999
	20	0.541	3.71	0.82	1.099	0.999
	40	0.386	3.43	1.22	1.073	0.997

We found that, for BTDA, the Avrami exponent, n , lies in the range of 3.43–4.22, and the values change at different cooling rates and BTDA amounts. For pristine PK, the n values range from 3.14 to about 4.52 as the cooling rate changes. In addition, we found that the Avrami exponents of PK/additives are much higher than that of PK. We consider that the non-isothermal crystallization mechanism of the compounds is complicated, suggesting that the introduction of BTDA significantly influences the mechanism of nucleation and crystal growth of PK. The Avrami exponent, $n = 3.14$ –4.52, is related to thermal nucleation with three dimensional growth. A high value of G_c indicates a high rate of crystallization and quantifies the crystallization rate constant after removing kinetic effects due to the non-isothermal conditions under which the crystallization experiments were performed. As expected, the values of G_c for PK/BTDA are lower than those of pure PK, and the differences become remarkable on increasing cooling rate. Again, this result suggests that the presence of BTDA inhibits crystallization.

Another widely used method is that proposed by Ozawa^[18], based on Avrami theory. The Ozawa model has also been used to describe the non-isothermal crystallization kinetics of polymers. This theory neglects several factors affecting the non-isothermal crystallization rate, and the Avrami equation is modified for non-isothermal treatment, assuming that the polymer melt was cooled at a constant rate and the mathematical derivation of

Evans^[19] is valid. According to the Ozawa model, the degree of conversion at temperature (T), the relative degree of crystallinity ($X(T)$), can be written according to Eqs. (3) and (4):

$$X(T) = 1 - \exp[-k_c/\phi^m] \quad (3)$$

$$\lg[-\ln(1 - X(T))] = \lg k_c - m \lg \phi \quad (4)$$

where m is the Ozawa exponent depending on the dimension of crystal growth, and k_c is a measure of the crystallization rate.

The Ozawa plots of $\lg[-\ln(1 - X(T))]$ versus $\lg \phi$ for PK and PK/BTDA are shown in Fig. 5. The dependence is not linear, and large curvature is observed in the plots. The experimental data indicate that the Ozawa equation is not suitable for describing the non-isothermal crystallization kinetics for PK and its compounds. Because non-isothermal crystallization is a dynamic process, the crystallization rate is not constant (it is a function of time and cooling rate), and the quasi-isothermal treatment of the Ozawa model is questionable. This result may arise due to secondary crystallization and the dependence of the fold length on temperature for PK^[20].

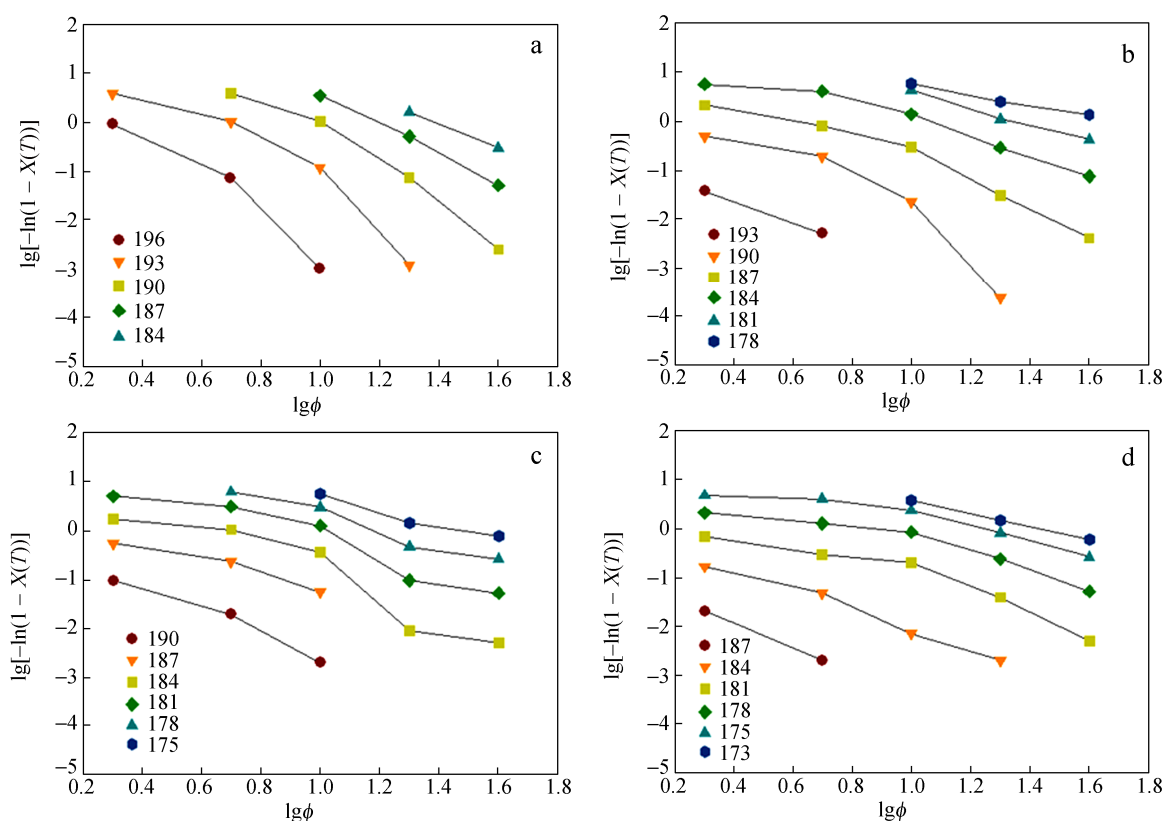


Fig. 5 Ozawa plot of $\lg[-\ln(1 - X(T))]$ versus $\lg \phi$ at several temperatures for (a) PK and PK with different BTDA contents: (b) 0.5 phr, (c) 1.0 phr and (d) 1.5 phr

To overcome the limitations of the current models for non-isothermal crystallization behavior, Liu *et al.*^[21] proposed the use of a combined Avrami and Ozawa model to describe the non-isothermal crystallization process, in which the degree of crystallinity is related to the cooling rate and crystallization time (or temperature). The relationship between cooling rate (ϕ) and crystallization time (t) can be built up at a given degree of crystallinity. This convenient kinetic model has been adopted to deal with the non-isothermal data of many polymer systems^[22–24].

The new kinetic equation of non-isothermal crystallization is developed by combining Eqs. (5) and (6):

$$\lg G_t + n \lg t = \lg K(t) - m \lg \phi \quad (5)$$

$$\lg \phi = \lg F(t) - a \lg t \quad (6)$$

where the kinetic parameter $F(t) = [K(t)/G_t]^{1/m}$ represents the value of the cooling rate to reach a defined relative crystallinity at a unit crystallization time, $K(t)$ is referred to the crystallization rate and a is the ratio of the Avrami exponent (n) to the Ozawa exponent (m).

Figure 6 shows the plots of the $\lg \phi$ versus $\lg t$ at the given relative crystallinity of PK and PK/BTDA. These plots yield a series of straight lines at a given relative crystallinity, suggesting that this analysis may be more effective in describing the non-isothermal crystallization kinetics of PK and PK/BTDA compounds than the Ozawa model. All plots show a good linear relationship ($r^2 > 0.98$), which also validates the success of the combined Avrami and Ozawa equations in this system. The kinetic parameter $F(t)$ and the exponent a can be estimated by the intercept and slope of these straight lines, respectively. The results for $F(t)$ and a are summarized in Table 3.

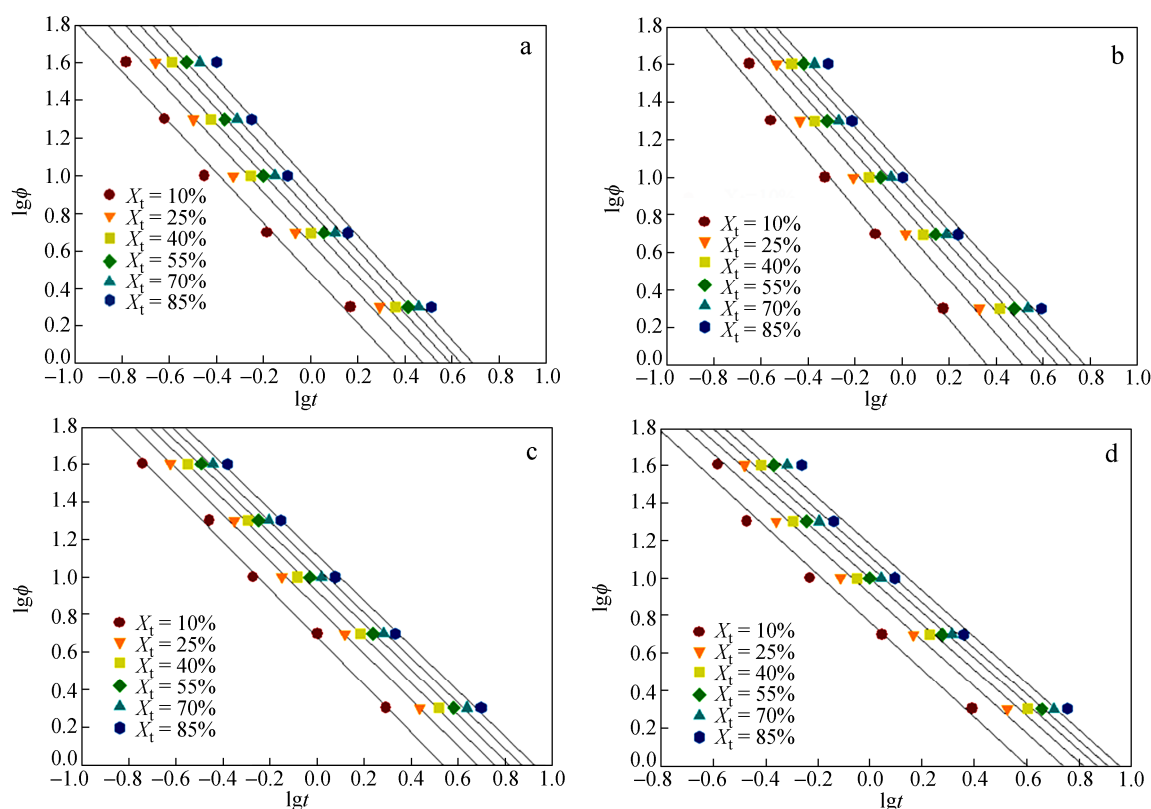


Fig. 6 Plots of the $\lg \phi$ versus $\lg t$ at the given relative crystallinity for (a) PK and PK with different BTDA contents: (b) 0.5 phr, (c) 1.0 phr and (d) 1.5 phr

It is apparent that the value of $F(t)$ increases with increasing relative crystallinity, indicating that, at unit crystallization time, a higher relative degree of crystallinity is obtained with a higher cooling rate. The value of $F(t)$ for PK/BTDA is higher than that of the pristine PK, indicating that the crystallization rate of PK decreases on addition of BTDA. Additionally, the values of a varied from 1.34 to 1.39 for PK and from 1.21 to 1.50 for PK/BTDA, which indicates that crystal growth and nucleation of PK are changed little by the addition of other materials.

Table 3 Kinetic parameters for the PK and PK/BTDA obtained from the combined Avrami-Ozawa equation

	$X(t)$ (%)	a	$F(t)$	r^2
PK	10	1.34	3.02	0.985
	25	1.34	4.39	0.984
	40	1.35	5.45	0.984
	55	1.36	6.46	0.984
	70	1.37	7.57	0.983
	85	1.39	9.11	0.980
PK/BTDA (0.5 phr)	10	1.50	3.45	0.985
	25	1.44	5.48	0.984
	40	1.41	6.96	0.983
	55	1.39	8.31	0.982
	70	1.38	9.73	0.981
	85	1.37	11.55	0.980
PK/BTDA (1.0 phr)	10	1.27	4.83	0.997
	25	1.23	6.92	0.999
	40	1.22	8.45	0.999
	55	1.21	9.84	0.999
	70	1.21	11.26	0.999
	85	1.21	13.15	0.998
PK/BTDA (1.5 phr)	10	1.27	5.83	0.983
	25	1.24	8.25	0.984
	40	1.22	9.94	0.983
	55	1.22	11.45	0.982
	70	1.22	13.04	0.981
	85	1.23	15.12	0.980

CONCLUSIONS

In summary, the melting temperature, crystallization temperature, and crystallization rate of PK were significantly affected by carboxylic acid and anhydride organic additives. A mechanism of interaction between PK and organic additives was also proposed. Regarding the quantity of additives with respect to the effect on the properties of PK, we found that BTDA was the most efficient material. The results of the WAXD analysis show that BTDA, CA, and PAA have less effect on the crystalline structure and the degree of crystallinity of PK. The crystallization temperature and rate of PK was easily controlled by using different additive loadings. On increasing the additive feed ratio, the crystallization rate of PK significantly reduced. The crystallization kinetics of PK/BTDA was also studied under non-isothermal conditions using Avrami, Ozawa, and combined Avrami-Ozawa equations. Among the three tested models, the Avrami and combined Avrami-Ozawa model proved to be both suitable and convenient to model the non-isothermal crystallization of PK and PK/BTDA compounds.

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