Non-isothermal Crystallization Behavior of Poly(ethylene terephthalate)/Poly(trimethylene terephthalate) Blends

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Summary

Non-isothermal crystallization behavior of Poly(ethylene terephthalate)/ Poly(trimethylene terephthalate) blends was investigated by XRD and DSC. By XRD spectra analysis, it could be concluded that PET and PTT crystals coexisted. They did not form the cocrystals due to different chemical structures. The Avrami equations modified by Jeziorny and Ziabicki's kinetic crystallizability analysis were employed to describe the non-isothermal crystallization process of PET/PTT blends. The results suggested that the entanglement of the two polymer chains decrease the crystallizability of PET and PTT in blend. The crystallization activation energies of the blend evaluated by the Friedman method also indicated that the presence of two components in the blends hinders the crystallization process of both components.

Introduction

Much attention has been focused on the development and investigation of binary polymer blends, which allow the combination of desirable properties of different polymers with exceptional advantages over the development of novel polymer materials. Most of them focused on the mixtures of two amorphous components, or mixtures of amorphous and crystalline components. However, polymer blends containing two crystalline components are less frequently discussed.

Both poly (ethylene terephthalate) (PET) and poly (trimethylene terephthalate) (PTT) are semicrystalline aromatic polyesters. PET is the most important polyester with satisfactory thermal stability and mechanical properties, which have been widely used as fibers, bottles, packages, etc for many years [1]. While PTT is a relative new polymeric material that developed by Shell Chemical Co. Since its commercial introduction in 1998, there has been an increased interest in PTT for fiber and engineering thermoplastic applications [2~4]. PTT has shown better tensile elastic recovery but lower modulus than PET [5]. Polymer blending is widely recognized as the most common method for developing new polymeric materials. It is also expected that blending of PET and PTT will offer an interesting route to combine the

complementary properties of both polymers. Opperman et al. [6] have prepared PET/PTT blend fibers by melt spinning. They found that PTT significantly improves recovery during cyclic deformation of PET fibers at a concentration of 10 wt%. The experimental results also revealed that PET/PTT blend fibers are dyed more easily than pure PET and PTT fibers. Choi et al. [7] investigated the effects of processing conditions on the thermal properties and the ester exchange interaction of PET/PTT blends. Tae et al. [8] confirmed that transesterification occurs between PTT and PET. They reported that crystallization of one component interferes with crystallization of other component in PET/PTT blends. Recently, Supaphol et al. [9] investigated the thermal, crystallization, mechanical, and rheological properties of PET/PTT blends systemically. In our recent work, the miscibility and melting behavior of PET/PTT blends had been investigated [10]. The blends exhibit a single composition-dependent glass transition temperature, which indicated that both components were miscible in the amorphous phase. The negative value of polymer–polymer interaction parameter, χ_{12}, calculated from equilibrium melting temperature depression of the PET component, also indicated the miscibility of PET/PTT blends in the melting state.

In practice, the production and processing of crystallizable polymer are often carried out under non-isothermal condition, such as melt-spinning, injection molding and extraction. Therefore, the investigation of non-isothermal behavior of polymers is theoretically and practically significant. According to our knowledge, no prior non-isothermal kinetics study has been reported on PET/PTT blends. The purpose of the present study is to investigate the non-isothermal crystallization behavior of PET/PTT blends.

Experimental

Materials

PET in pellet form was kindly supplied by Shanghai Petrochemical Co.Ltd. Its intrinsic viscosity (IV) is 0.76 dL/g measured in a 60:40 wt% solvent of phenol and 1,1,2,2-tetrachloroethane at 30°C. PTT (Corterra CP509201, Shell Chemicals) in pellet form with an intrinsic viscosity of 0.92 dL/g was used in this study.

Samples preparation

Before blending, both polymers pellets were dried at 150°C for 5h in an air oven to remove moisture in order to minimize the possibility of hydrolysis. The samples of PET/PTT blends with different weight ratio compositions (20/80, 40/60, 50/50, 60/40 and 80/20), were prepared in a 30-mm co-rotating twin screw extruder (TE-34) with an L/D of 28, a barrel temperature ranging from 235°C to 280°C, and a screw speed of 40 rpm. The strand from the extruder was quenched in a water bath and cut into chips.

Characterizations

Non-isothermal crystallization kinetics of PET, PTT and their blends with various compositions were carried out *in situ* by a differential scanning calorimeter (DSC) (Perkin-Elmer Pyris 1 DSC). Both temperature and heat flow were calibrated by indium standard. All samples were dried in a vacuum at 50°C for 12 h before the

measurements. To minimize thermal lag between the polymer sample and the DSC furnace, thin films of the samples about 200 μm were melt-pressed by a compression molding machine. A disc-shaped specimen weighting around 5 mg, which was cut from the as-prepared films was sealed in the aluminum pan and heated above 280°C for 5 min in order to eliminate any residual crystals. Then, the melt was cooled at selected constant rates Φ (ranging from 5 to 40°C/min). The exothermal curves of heat flow as a function of temperature were recorded and analyzed. All DSC measurements were performed under a nitrogen purge and each sample was used only once.

The X-ray diffraction (XRD) was performed on the samples prepared as thin discs in the DSC. The XRD spectra were conducted on a Philips X'Pert PRO X-ray diffractometer using CuKα radiation of $\lambda = 1.5406$ Å. Data were collected over the range $2\theta = 7.5{\sim}40°$ in the fixed time mode with a step interval of 0.02°.

Results and discussion

X-ray diffraction spectra analysis

The end-crystalline morphology of PET, PTT and their blends after non-isothermal crystallization was investigated by XRD. The samples were first melted at 280°C, followed by a cooling rate of 10°C/min to room temperature. The X-ray diffraction patterns for PET, PTT and their blends are shown in Figure 1.
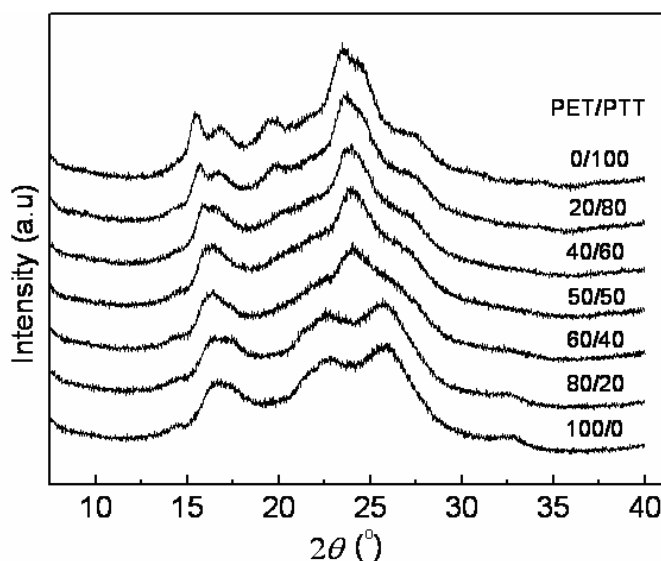

Fig.1 XRD patterns for PET, PTT and their blends cooled to room temperature at a cooling rate of 10°C/min

The crystalline structures of PET and PTT are identified to be triclinic [11~13]. The neat PET showed peaks at scattering angles at 2θ values of 16.6, 17.4, 22.9, 25.9, and 32.7°. These peaks correspond to the $(0,\bar{1},1)$, $(0,1,0)$, $(1,\bar{1},0)$, and $(1,0,1)$ scattering

planes, respectively [14]. As to PTT, it showed peaks at scattering angles at 2 θ values of 15.4, 16.9, 19.8, 23.4, 24.1 and 27.2°, corresponding to the (0,1,0), (0,$\bar{1}$,2), (0,1,2), (1,0,2), (1,$\bar{1}$,3) and (1,0,3) scattering planes, respectively [15]. These data are in good agreement with those reported for the PET and PTT crystal unit cells.

The peaks of the PET/PTT blends could be indexed by the neat PET and PTT, respectively. Since the XRD patterns of PET/PTT blends showed no new peaks, it could be concluded that PET and PTT crystals coexisted. They did not form the cocrystals due to different chemical structures. In analyzing XRD data, the background scattering was subtracted from total intensity curve. The total degree of crystallinity X_c is then obtained from [16]

$$X_c = \frac{I_c}{I_c + kI_a} \tag{1}$$

where I_a is the intensity of amorphous scattering, I_c is the intensity of the crystalline diffraction, and k is the correct factor, respectively. This procedure involves the separation of X-ray scattering intensities into amorphous and crystalline components. Figure 2 shows the total degree of crystallinity as a function of PTT content.
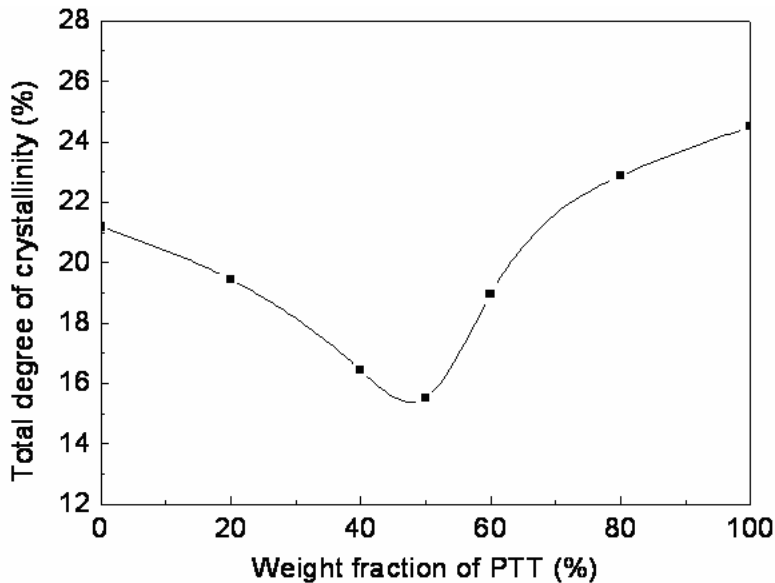

Fig.2 Total degree of crystallinity as a function of PTT content

From Fig.2 we can see that the total degree of crystallinity is gradually reducing and then increasing with the increase of the PTT component. The total degree of crystallinity of PET/PTT blends changes gradually between the corresponding values of pure components. According to the above analysis, each polymer crystallizes individually and contributes to the total crystallinity. But the total crystallinity attained is lower than the linearly added contributions of the components and the 50/50 sample

showed the lowest value. In the crystallization process of the PET/PTT blends, the interpenetrating and entangling of the two kinds polymer chains reduce the segmental mobility and hinder the ordered arrangement of the PET and PTT polymer chains to form their own crystals respectively. Increasing the degree of entanglement between the chains of PET and PTT can decrease the total crystallinity. It is obviously that the degree of entanglement between the chains of PET and PTT is highest in the 50/50 sample. That is to say, the presence of two components in the blends hinders the crystallization process of both components. Similar phenomenon has also been reported in other crystalline/crystalline polymer blends [17].

Non-isothermal crystallization kinetic analysis by Jeziorny

The typical crystallization exotherms of 50/50 PET/PTT blend at different cooling rates were presented in Figure 3.
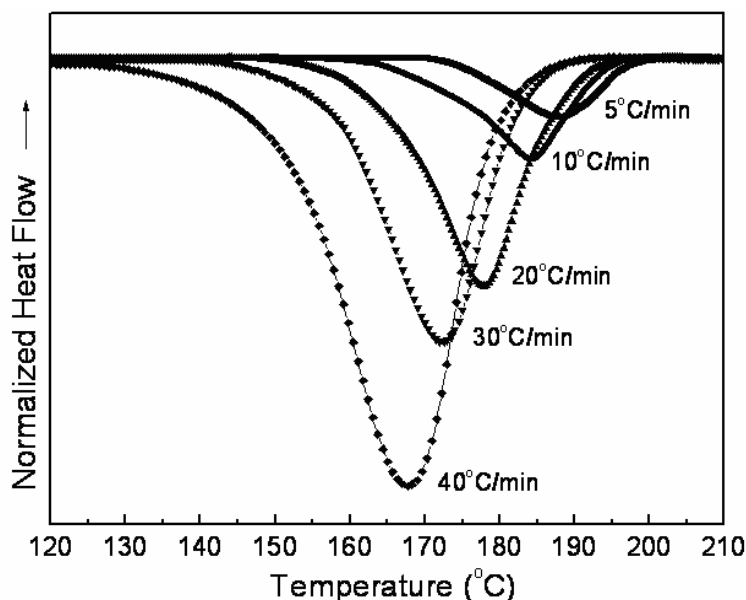

Fig.3 Non-isothermal crystallization exotherms of 50/50 PET/PTT blend at different cooling rates

The single crystallization exotherm observed for each cooling rate indicated that both PET and PTT crystallized simultaneously. In addition to that, as is usually observed, increasing the cooling rate shifts the crystallization peak to a lower temperature. Similar behavior was also been observed for blends of other compositions studied. From these exotherms, some useful data can be obtained for describing their nonisothermal crystallization behavior, such as the peak temperature (T_p), the half-time of crystallization ($t_{1/2}$) and the crystallization enthalpies ΔH; values of the parameters determined are listed in Table 1.

Table 1 Non-isothermal crystallization kinetic parameters of PET/PTT blends

PET/PTT	Φ(°C/min)	T_p(°C)	ΔH(J/g)	n	Z_t	Z_c	$t_{1/2}$ (min)
100/0	5	214.19	-44.66	4.01	0.020	0.456	2.149
	10	205.72	-41.45	4.26	0.217	0.858	1.265
	20	200.70	-39.68	4.14	4.102	1.073	0.723
	30	194.86	-36.62	4.58	13.062	1.089	0.538
	40	193.58	-34.47	4.12	46.009	1.100	0.496
80/20	5	212.28	-34.50	4.13	0.0175	0.446	2.567
	10	207.71	-33.83	4.98	0.0499	0.745	1.656
	20	200.79	-32.33	4.60	1.185	1.009	0.878
	30	191.79	-31.98	4.13	4.035	1.048	0.636
	40	188.32	-28.42	4.96	15.161	1.070	0.553
60/40	5	199.48	-29.91	4.92	0.0016	0.276	3.368
	10	194.97	-25.22	4.30	0.072	0.768	1.679
	20	185.23	-24.39	4.18	0.301	0.942	1.165
	30	180.98	-20.91	4.24	2.803	1.035	0.717
	40	172.93	-13.66	4.35	4.585	1.039	0.603
50/50	5	188.21	-27.90	4.19	0.0014	0.268	4.212
	10	184.68	-27.15	4.01	0.047	0.736	1.906
	20	177.93	-28.78	4.74	0.209	0.925	1.292
	30	172.56	-26.77	4.65	1.513	1.014	0.815
	40	167.66	-24.98	4.43	3.026	1.028	0.707
40/60	5	184.89	-41.03	4.66	0.008	0.382	2.451
	10	182.65	-36.03	4.49	0.111	0.802	1.494
	20	174.95	-35.91	4.19	1.108	1.005	0.909
	30	169.63	-35.87	4.36	5.150	1.056	0.645
	40	161.76	-33.53	5.45	42.131	1.098	0.586
20/80	5	187.90	-45.202	5.15	0.011	0.404	2.357
	10	183.63	-42.518	4.27	0.494	0.932	1.066
	20	177.93	-39.519	4.12	4.446	1.077	0.656
	30	173.59	-38.831	4.60	17.132	1.099	0.509
	40	168.97	-37.546	4.26	42.131	1.098	0.340
0/100	5	185.09	-47.968	4.79	0.027	0.486	1.947
	10	179.04	-46.523	4.22	1.064	1.006	0.891
	20	170.98	-45.958	5.20	6.523	1.098	0.635
	30	165.70	-45.742	4.23	30.575	1.121	0.399
	40	161.08	-43.533	4.11	45.809	1.100	0.337

As it is well known, higher cooling rate results in lower T_p, which in turn results in higher super-cooling. Thus, crystallization rates are enhanced. In addition to that, ΔH is gradually decreased due to the less crystallites formed in the blend with increasing cooling rate.

The relative crystallinity X_t as a function of crystallization temperature is defined as:

$$X_t = \frac{\int_{T_0}^{T}(dH/dt)\,dT}{\int_{T_0}^{T_\infty}(dH/dt)\,dT} \tag{2}$$

where T_0 and T_∞ represent the onset and end temperatures of crystallization, respectively. The development of X_t with crystallization temperatures at various cooling rates is presented in Figure.4. Generally, all these curves had the same sigmoidal which indicated that only the lag effect of cooling rate on crystallization were observed for these samples.
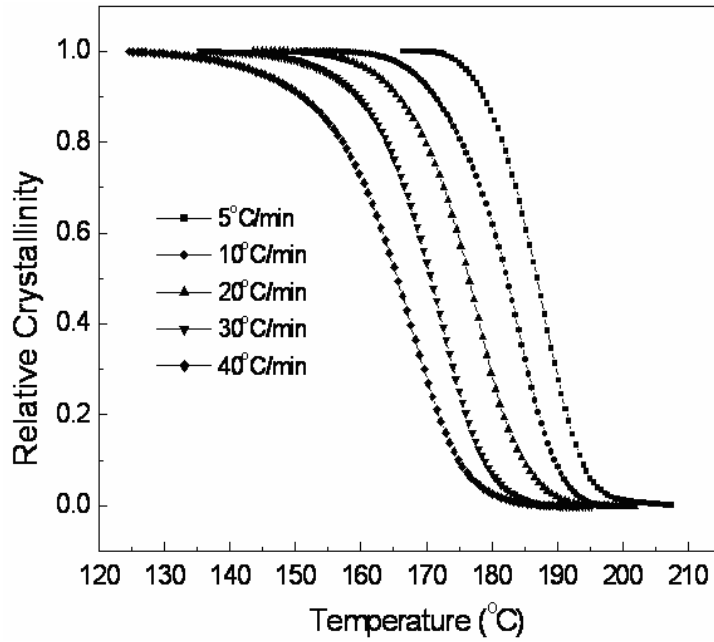

Fig.4 Variation of relative crystallinity with crystallization temperature (50/50 PET/PTT)

During the non-isothermal melt crystallization process, the relation between crystallization time t and the corresponding temperature is given by the following equation:

$$t = \frac{T_0 - T}{\Phi} \qquad (3)$$

According to eq.(3), the x-axis parameters in Figure 4 could be transformed in to crystallization time t shown in Figure 5.

Through Fig.5, the $t_{1/2}$ value can be obtained and also listed in Table 1. The $t_{1/2}$ data decrease with increasing cooling rates, reveal that the higher the cooling rate, the shorter the time of crystallization. Compared the values of $t_{1/2}$ of PET/PTT blends with those of pure PET and PTT at a given cooling rate; it is clear that for PET-rich blends, the $t_{1/2}$ value increased with the addition of PTT component in binary blend, which indicates a decrease of crystallization rate. For PTT-rich blends, a similar phenomenon has also been found and the 50/50 blend showed the lowest crystallization rate.
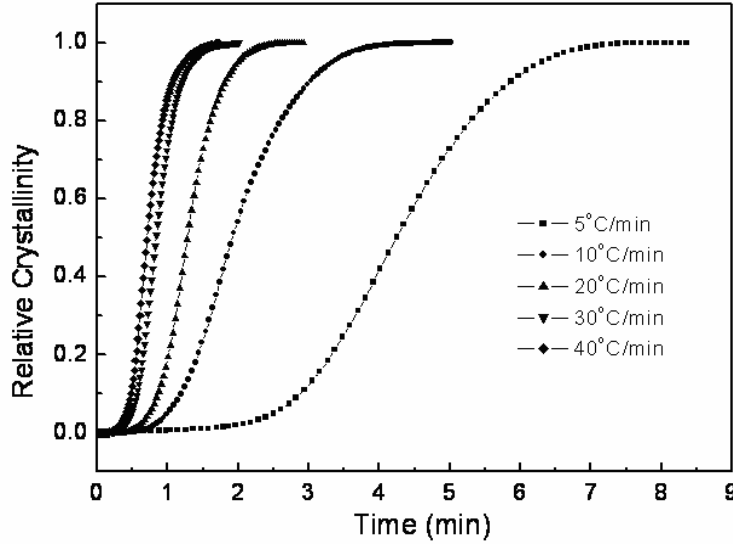
Fig.5 Variation of relative crystallinity with crystallization time (50/50 PET/PTT)

The kinetic parameters of nonisothermal crystallization were determined on the basis of the simplified assumption that crystallization occurs under constant temperature. In this case, the Avrami equation can be used [18]:

$$1 - X_t = \exp\left(-Z_t t^n\right) \tag{4}$$

Or

$$\log\left[-\ln\left(1 - X_t\right)\right] = \log Z_t + n \log t \tag{5}$$

where the Avrami exponent n is a mechanism constant, which is dependent on the type of nucleation and growth process parameters, and the parameter Z_t is a composite rate constant that involves both nucleation and growth rate parameters. The exponent (n) and parameter (Z_t) can be obtained from the slope and intercept of the line in the plot of $\log\left[-\ln\left(1 - X_t\right)\right]$ versus $\log t$ (Figure 6).

As with many experimental observations, all of these curves are separated into two sections: the primary and secondary crystallization stages. At the secondary stage, the straight line tends to deviate from the primary crystallization stage. The results indicate that there exists a secondary crystallization stage in the non-isothermal crystallization process for PET/PTT blends [19].

Considering the nonisothermal character of the process investigated, Jeziorny presented the final form of the parameter characterizing the kinetics of nonisothermal crystallization as follows [20]:

$$\log Z_c = \log Z_t / \Phi \tag{6}$$

The results, obtained from Avrami plots and the Jeziorny method, are also listed in Table I. The exponent n varied from 4.01 to 4.58 for PET, from 4.11 to 5.20 for
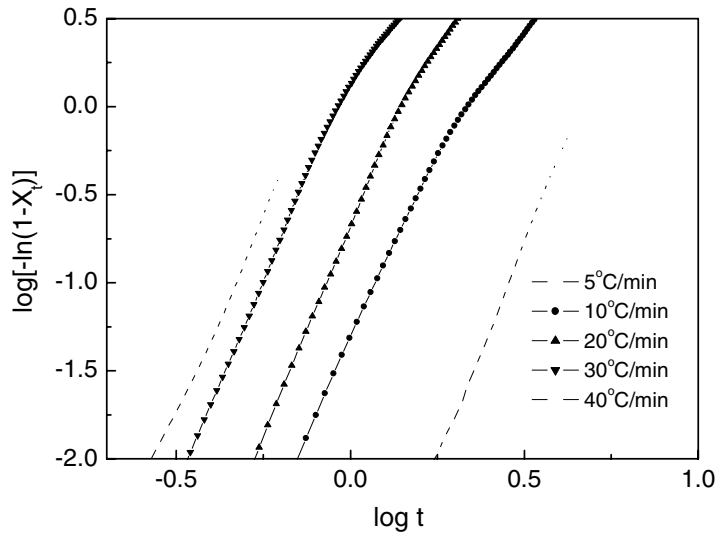
Fig.6 Plots of $\log\left[-\ln\left(1-X_t\right)\right]$ versus $\log t$ (50/50 PET/PTT)

PTT, and from 4.01 to 5.45 for PET/PTT blends. This result of the values of exponent $n > 4$ at various cooling rates may due to the spherulites' impingement and crowding, or the complicated nucleation types and growth form of spherulites [21]. For the nonisothermal crystallization, the rate parameter Z_c decreased with increasing cooling rate. The change of Z_c values indicated the effect of dominance of both nucleation and growth process [22].

Ziabicki's kinetic crystallizability analysis

Ziabiki first investigated the kinetics of nonisothermal crystallization in 1967 [23,24]. He developed a theory based on the assumption that crystallization can be presented by means of the equation for first order kinetics as following:

$$dX_t/dt = \left(1 - X_t\right)K(T) \tag{7}$$

where the rate constant $K(\mathrm{T})$, defined empirically through the reciprocal half-time of crystallization, is temperature-dependent. The change of rate constant as a function of temperature is illustrated by a curve resembling a Gaussian. The curve is described by:

$$K(T) \approx K_{max} \exp\left[-4\ln 2\frac{\left(T - T_{max}\right)^2}{D^2}\right] \tag{8}$$

where K_{max} is the maximum value of the rate constant corresponding to the temperature T_{max}; D is the half-width of the crystallization curve. The kinetic crystallizability (G) can be obtained from:

$$G = \int_{T_g}^{T_m} K(T)dT = \left(\pi/\ln 2\right)^{1/2}K_{max}\,D/2 \tag{9}$$

where T_g is the glass transition temperature of the polymer and T_m is the melting temperature of the polymer. The kinetic crystallizability (G) characterizes the degree of transformation obtained over the entire crystallization range ($T_g \sim T_m$) with a given cooling rate. Considering the influence of cooling rate during nonisothermal crystallization, Jeziorny proposed that the final corrected form of this parameter will thus be described as follows [20]:

$$G_c = \frac{G}{\Phi} \tag{10}$$

Calculation of G_c parameter was made possible by knowing the values of K_{max} and D. The half-width D can be easily determined from the crystallization thermogram. The K_{max} value, corresponding to temperature T_{max}, at which the crystallization rate is the maximum, can be calculated by the following equations:

$$K_{max} = C_k \left(t_{max} \right)^{-1} \tag{11}$$

$$C_k = \frac{\int_{t_0}^{t_{max}} V_c(t)\,dt}{\int_{t_{max}}^{t_e} V_c(t)\,dt} \tag{12}$$

$V_c(t)$ represents an exothermic DSC thermogram, t_0 and t_e are the oneset and end time, respectively. t_{max} is the time taken from the start of crystallization until reaching the maximum rate.

The parameters characterizing the nonisothermal kinetic crystallizability of PET/PTT blends examined are listed in Table 2.

Table 2 Parameters characterizing the kinetic crystallizability of nonisothermal crystallization of PET/PTT

Φ (°C/min)	100/0			80/20			60/40			50/50		
	D(K)	K_{max}	G_c	D(K)	K_{max}	G_c	D(K)	K_{max}	G_c	D(K)	K_{max}	G_c
5	8.3	0.49	0.86	7.1	0.43	0.65	10.2	0.23	0.51	12.1	0.28	0.73
10	9.6	0.89	0.91	7.7	1.11	0.91	12.1	0.45	0.58	13.9	0.34	0.51
20	12.1	1.05	0.68	9.7	1.12	0.58	15.7	0.71	0.59	15.1	0.96	0.77
30	14.3	1.62	0.82	11.9	1.94	0.82	18.9	1.07	0.72	16.3	1.05	0.61
40	15.2	1.93	0.78	13.2	2.02	0.71	21	1.13	0.63	19.2	1.04	0.53
Average			0.81			0.73			0.61			0.63

Φ (°C/min)	40/60			20/80			0/100		
	D(K)	K_{max}	G_c	D(K)	K_{max}	G_c	D(K)	K_{max}	G_c
5	8.3	0.40	0.71	8.6	0.61	1.11	7.6	0.75	1.21
10	10.3	0.57	0.62	9.3	0.83	0.82	8.2	1.12	0.98
20	13.1	1.31	0.91	11.5	1.49	0.91	8.9	1.94	0.92
30	15.9	1.49	0.84	13.1	2.17	1.01	9.3	3.42	1.13
40	18.1	1.64	0.79	14.3	1.99	0.76	10.6	3.58	1.01
Average			0.77			0.92			1.05

G_c can be effectively used to characterize the kinetics of nonisothermal crystallization because values of this parameter do not depend on the cooling rate of the crystallization process. Therefore one obvious advantage of this parameter is its nondimensional character. From Table 2, the average G_c values of pure PTT and PET are 1.05 and 0.81, respectively. It is obvious that PTT showed the higher crystallizability than that of PET. Moreover, with the addition of another component, the crystallizability of the blend decreased and the 50/50 blend showed the lowest G_c value. Kinetic crystallizability has been shown to be largely determined by the mobility of the polymer chains [25, 26]. Our previous work revealed that the two components of PET and PTT in the blend are mixed more uniformly, which results in a higher level of entanglement between the chains of PET and PTT in the melting state [10]. Thus, the entanglement of the two polymer chains will reduce the rate of incorporation of crystallizable chain segments into the crystallites to form PET and PTT crystals, respectively.

Crystallization Activation Energy

In order to obtain the reliable values of the effective activation energy on the melt cooling process, Friedman [27] and Vyazovkin [28] developed differential isoconversional method and integral isoconversional method, respectively. Here, the crystallization activation energy ΔE could be determined by using the isoconversional method developed by Friedman, as follows:

$$\ln\left(\frac{dX}{dt}\right)_X = F(X) - \frac{\Delta E_X}{RT_X} \tag{13}$$

where $(dX/dt)_X$ is the instantaneous crystallization rate, as a function of time at a given relative crystallinity X, and T_X is the temperature related to the given relative crystallinity X, for different cooling runs from the melt, $F(X)$ is a function correlated with X. From Equation (13), straight lines of $\ln(dX/dt)_X$ as a function of T_X for a series of given X values can be obtained. The activation energy ΔE can be calculated from the slope $-\Delta E/R$. The obtained ΔE values at the given relative crystallinity X are listed in Table 3.

Table 3 Crystallization activation energy ΔE ontained by Friedman method

X	ΔE (kJ.mol^{-1})						
	100/0	80/20	60/40	50/50	40/60	20/80	0/100
0.1	-139.3	-121.9	-110.3	-101.7	-131.1	-168.2	-182.2
0.3	-110.7	-101.8	-87.6	-85.9	-100.3	-124.8	-138.9
0.5	-95.3	-78.5	-69.4	-69.1	-79.9	-92.3	-113.1
0.7	-79.4	-65.1	-59.2	-56.3	-68.2	-72.5	-88.6
0.9	-42.1	-38.1	-21.9	-20.6	-31.7	-52.7	-69.3
Average	-93.3	-81.0	-69.6	-66.7	-82.2	-102.1	-118.4

It should be noted that the lower the ΔE value, the higher the crystallization ability of the polymer sample. According to Table 3, the ΔE values were found to increase with the relative crystallinity, suggesting that as the crystallization proceeded it was more difficult for PET, PTT and PET/PTT blends to crystallize. It can also be

found that the average ΔE value is gradually increasing and then reducing with the increase of the PTT component. The 50/50 sample showed the highest value. ΔE is the activation energy required to transport molecular segments to the crystallization surface. The variation of ΔE indicates that the addition of the other component makes the transportation of chains to a growing crystal surface more difficult. It also provided evidence that the presence of two components in the blends hinders the crystallization process of both components.

Conclusion

By XRD spectra analysis, it could be concluded that PET and PTT crystals coexisted. They did not form the cocrystals due to different chemical structures. The total degree of crystallinity of PET/PTT blends changes gradually between the corresponding values of pure components.

The Avrami equations modified by Jeziorny and Ziabicki's kinetic crystallizability analysis were employed to describe the nonisothermal crystallization process of PET/PTT blends. With the addition of another component, the $t_{1/2}$ value increased and the crystallizability of the blend decreased. It is suggested that the entanglement of the two polymer chains will reduce the rate of incorporation of crystallizable chain segments into the crystallites to form PET and PTT crystals, respectively.

The crystallization activation energies of the blend were evaluated by the Friedman method. The 50/50 sample showed the highest value. The result also indicated that the presence of two components in the blends hinders the crystallization process of both components.

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