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# Nonisothermal Crystallization Kinetics of Poly(ethylene terephthalate) and Blends of Polystyrene and Nylon 6

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Differential scanning calorimeter (DSC) has been used to study nonisothermal crystallization kinetics of nucleation and growth. These studies were done by extending the Ozawa equation for crystallization obtained by cooling poly(ethylene terephthalate) (PET) homopolymer and its blends with polystyrene and nylon 6 at variable rates. PET crystallization proceeds by random nucleation with two-directional diffusion-controlled growth. The apparent activation energy and nucleation facilitation are greater in blends.

**Keywords:** DSC; Crystallization kinetics; Polymer blends; Poly(ethylene terephthalate); Nylon 6; Polystyrene

## INTRODUCTION

The prediction of nonisothermal crystallization kinetics remains a longstanding scientific and technical objective. Nakamura<sup>[1]</sup> and Malkin<sup>[2]</sup> attempted to generalize previous kinetic theories based on Avrami analysis to nonisothermal conditions. Ozawa<sup>[3]</sup> extended this to the nonisothermal crystallization kinetics of poly(ethylene terephthalate) (PET). He has attributed the discrepancy between the value of  $n$  (Avrami exponent) by dynamic and isothermal methods to

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slow secondary crystallization in the isothermal method. Nadkarni<sup>[4]</sup> has studied the crystallization kinetics of poly(phenylene sulfide) and concluded that nucleation is a homogeneous process.

In this paper nonisothermal kinetics of nucleation and growth are investigated for PET homopolymer and PET in blends with 50% polystyrene and 50% nylon 6 using the extended Ozawa<sup>[3]</sup> method. Attempts have also been made to study other kinetic parameters, such as activation energy ( $E_a$ ) and crystallization half time ( $t_{1/2}$ ), since the effect of blending on crystallization kinetics is expected to be influenced by the mobility of chains.

## EXPERIMENTAL

### Materials

The source and thermal characteristics of PET, PS, nylon 6 is given in Table I and sample preparation of 50% PS and 50% nylon 6 in PET is given elsewhere.<sup>[5]</sup>

### Thermal Analysis

Mettler DSC 30 with a TC 11 TA processor (Toledo, Switzerland) was used for thermal characterization. Cooling rates of 5, 7, 10, 12 and 15 K/min were used. Prior to every run the sample was melted by heating to a temperature (300°C) higher than the maximum melting temperature without thermal degradation and then cooling under a controlled rate to obtain nonisothermal crystallization parameters. Melting parameters were obtained from re-heat scans of these non-isothermally crystallized samples.

## RESULTS AND DISCUSSIONS

The plot of the logarithm of cooling rates against peak temperature for PET and its blends is linear as shown in Figure 1, which show that the crystallization of PET, as well as in blends, is a single-step exothermic reaction.

TABLE I Source, thermal characteristics and solvent/nonsolvents used in purification of polymers

<i>Polymer</i>	<i>Source</i>	<i>Glass transition temperature, °C</i>	<i>Melting temperature °C</i>	<i>Solvent/nonsolvent</i>
PET	DCL Polyesters, Nagpur, Maharashtra, India	77.00	264.0	phenol 1,1,2,2-tetrachloroethane (60:40)/acetone
Nylon 6	Garware Nylons, Pune Maharashtra, India	55.00	225.0	<i>m</i> -cresol/ethanol
Polystyrene	Polychem, Mumbai Maharashtra India	90.00	—	toluene/methanol

Phenol, 1,1,2,2-tetrachloro ethane (TCE), *m*-cresol, acetone, toluene, methanol and ethanol were procured from Sisco Research Laboratory, Mumbai, Maharashtra, India with minimum assay of 99%. Phenol was distilled prior to use.

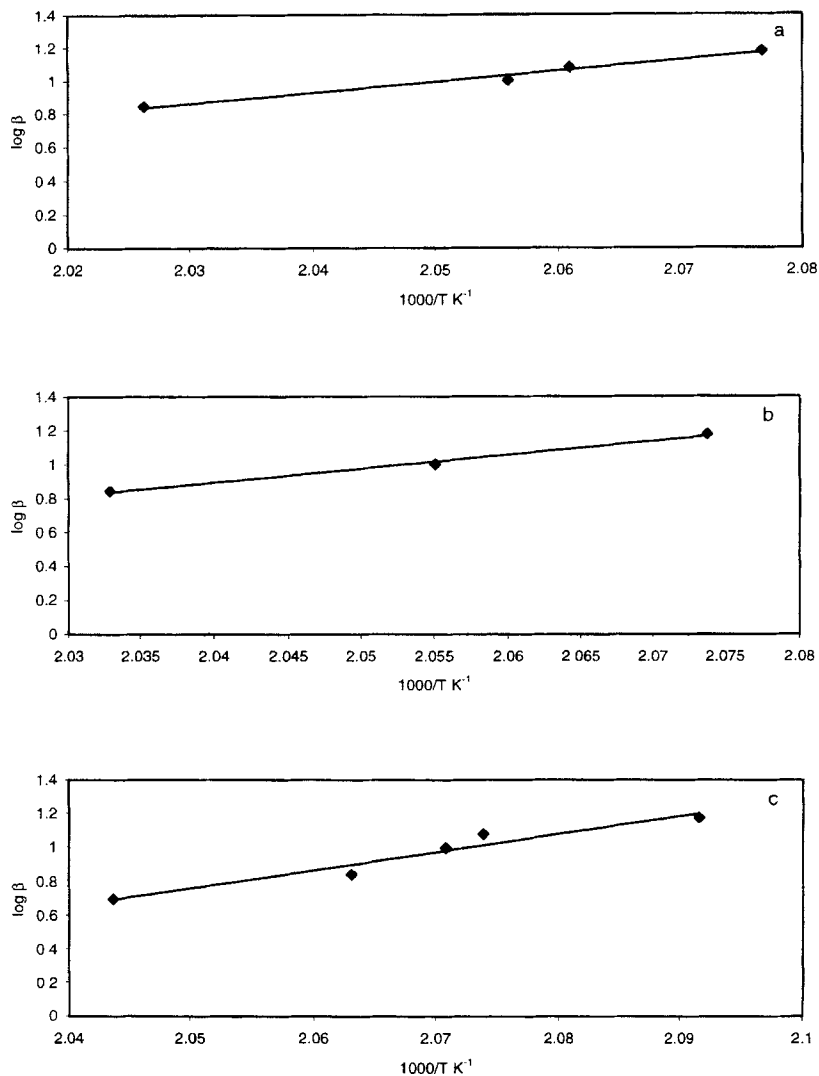


FIGURE 1 A plot of  $\log$  program rate *versus* peak temperature for PET blends: (a) pure PET, (b) 50% PS blend, (c) 50% nylon 6 blend.

### Calculation of Kinetic Parameters

The variable program rate method of Ozawa<sup>[6-9]</sup> has been employed to calculate the kinetic parameters. From the slope of the plot of

logarithm of program rate *versus* the peak temperature (Fig. 1), activation energy ( $E_a$ ) was calculated using the following equation: <sup>[10, 11]</sup>

$$E_a \cong 2.19R \cdot \{d \log \beta / d(1/T)\} \quad (1)$$

where  $R$  is the gas constant,  $\beta$  is the program rate (K/min), and  $T$  is the peak temperature. Using the activation energy ( $E_a$ ), the pre-exponential factor ( $A$ ) was computed for all sets of data and its average value used to calculate the specific rate constant ( $k$ ) and half-life time ( $t_{1/2}$ ) for a series of temperatures of interest as shown in Table II. Table II shows that during crystallization, activation energy for PET in all its blends as compared to pure PET increases. This behavior may be due to changes in the dynamics of PET crystallization because of other blend components <sup>[12]</sup> and can be related to both the potential of formation of a nucleus of critical size (nucleation) and to the transfer of polymer across the melt crystal interface (growth). In blends, other components acts as a solvent and thus activation energy changes. Furthermore, as the crystallization temperature increases, the rate constant ( $k$ ) increases and crystallization half-time ( $t_{1/2}$ ) decreases

TABLE II Effect of blending on crystallization kinetics of PET

Sample	Crystallization temp. (K)	$k$ , ( $\text{min}^{-1}$ )	$t_{1/2}$ (h)	$n$	$E_a$ ( $\text{kJ mol}^{-1}$ )
pure PET	480	0.39	1.76	2.67	104.6
	481	0.42	1.66	2.76	
	482	0.44	1.58	2.86	
	483	0.46	1.50	2.93	
	484	0.49	1.41	3.07	
	485	0.49	1.41	3.23	
	486	0.55	1.27	3.41	
	481	0.48	1.46	3.05	
50% PS blend	482	0.51	1.36	3.18	140.9
	483	0.55	1.26	3.16	
	484	0.59	1.17	3.20	
	485	0.63	1.09	3.36	
	486	0.68	1.02	3.51	
50% nylon 6 blend	480	0.65	1.06	2.35	196.2
	481	0.72	0.6	2.09	
	482	0.80	0.87	2.17	
	483	0.88	0.79	2.22	
	484	0.97	0.71	2.19	
	485	1.09	0.64	2.21	
	486	1.20	0.58	2.39	

for pure PET as well as for blends. A mere 5K change in crystallization temperature from 481 to 486K results in about a 28% change in crystallization half time for pure PET, about 30% for PET/50% PS blends, and about 45% for PET/50% nylon 6 blends. This decrease in half time is not only temperature dependent but varies with the composition of the blend and the nature of the other component. Change in crystallization half time over a particular temperature range is found to reach a maximum (45%) for the crystalline/crystalline blend system and is least for the homopolymer system.

### Avrami Exponent

The linear form of the Ozawa equation <sup>[3]</sup> is

$$\log \{-\ln(1 - \alpha(T))\} = \log X_c(T) - n \log \beta \quad (2)$$

where  $\alpha(T)$  is the mass fraction of crystallized material at temperature  $T$ ,  $\beta$  is the cooling rate and  $X_c(T)$  is the cooling crystallization function. A plot of fractional crystallization *versus* temperature for samples cooled at four different cooling rates is shown in Figure 2, which exhibits a shift in inflection point with cooling rate. From these plots, the values of  $\alpha$  at temperature  $T$  for different cooling rates were determined and used to obtain the Ozawa plot which is shown in Figure 3. The kinetic parameters  $n$  and  $X_c(T)$  have been estimated from the slope and intercept of Figure 3, respectively.

The values of  $n$  are tabulated in Table II. From Table II, the value of  $n$  changes, though marginally, with temperature. This observed phenomenon may be attributed to factors such as time-dependent nucleation, variant growth rate constants, combination of homogeneous and heterogeneous nucleation, *etc.* Fractional values of  $n$  may be expected mathematically, if certain constraints are imposed such as diffusion controlled growth.<sup>[13]</sup> Because the value of Avrami exponent for PET and PET in blends lie between 2 and 3 ( $2 < n < 3$ ), two-directional diffusion-controlled growth with homogeneous and heterogeneous nucleation is thought to be the probable mechanism of crystallization, considering the effect of blending on growth geometry.

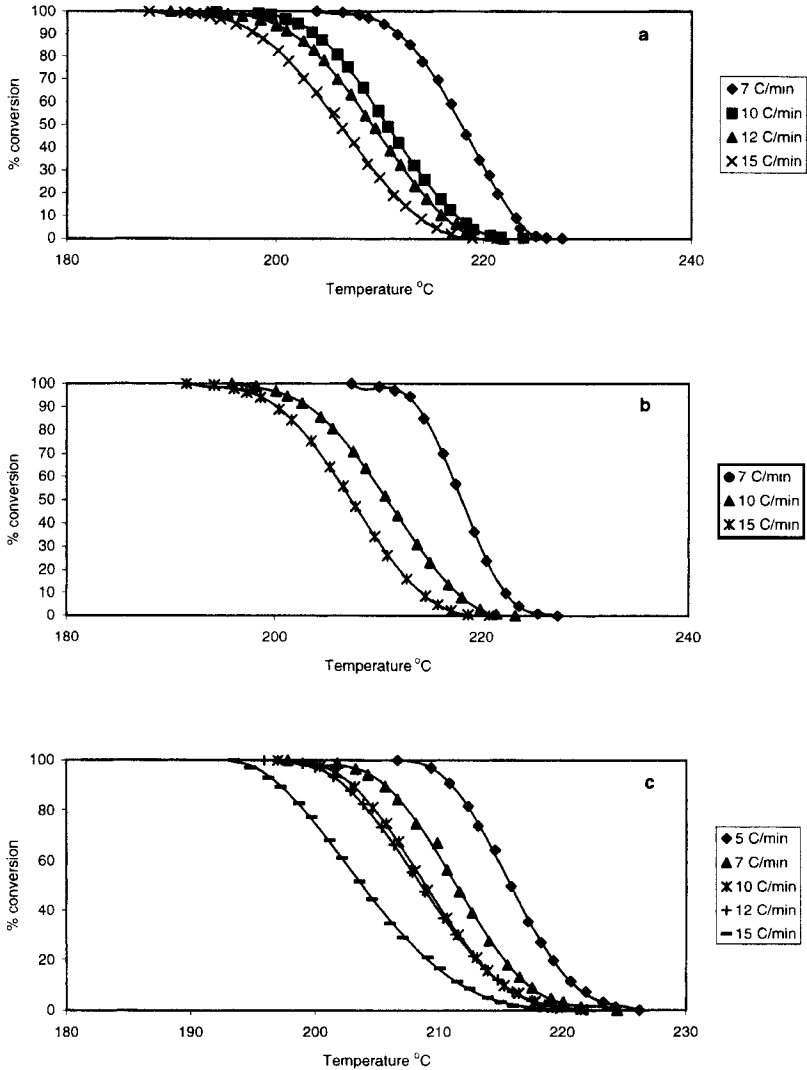


FIGURE 2 Conversion data for PET blends at variable cooling rates: (a) pure PET, (b) 50% PS blend, (c) 50% nylon 6 blend.

### Nucleation Related Parameter

For a coherent surface nucleation process, the nucleation controlled linear growth rate ( $G$ ) in direction normal to the surface may be



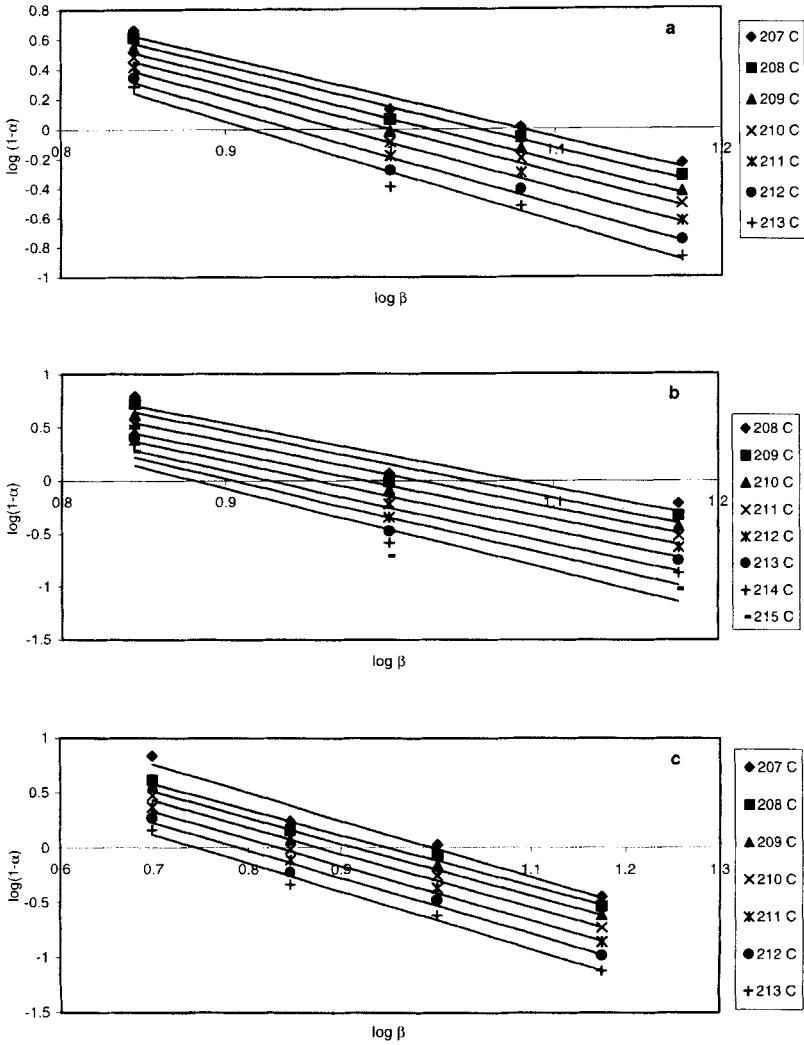


FIGURE 3 Avrami plots for nonisothermal crystallization: (a) pure PET, (b) 50% PS blend, (c) 50% nylon 6 blend.

given by <sup>[14]</sup>

$$G = bN/N_A \tag{3}$$

where  $b$  is the thickness of the nucleus,  $N$  is the rate of nucleation, and  $N_A$  is Avagadro's number. This relationship leads to an equation for

growth rate at crystallization temperature:

$$G = bk_B T/h \cdot \exp[-(\Delta F + \Delta\phi)/k_B T] \quad (4)$$

where  $\Delta\phi$  is free energy required to form a nucleus with critical size,  $\Delta F$  is the free energy of activation for diffusion of molecules across the phase boundary, and  $k_B$  is Boltzmann's constant. In case of a two-dimensional coherent surface, the nucleation term  $\Delta\phi/(k_B T)$  has the form  $(K_g/T\Delta T f)$ , where  $\Delta T = (T_m - T)$ , being the degree of undercool and  $f$  is a correction factor that takes into account the decrease of heat of fusion with the crystallization temperature, *i.e.*,  $f = 2T/(T_m + T)$ ;  $K_g$  is related to the lateral ( $\sigma$ ) and fold surface ( $\sigma_e$ ) free energies of the surface nucleation and is a nucleation related parameter.

Nonisothermal crystallization kinetics may be characterized by<sup>[14]</sup>

$$1/t_{1/2} = (1/t_{1/2})_o \cdot \exp(-\Delta F/k_B T) \cdot \exp[(-K_g/T\Delta T f)] \quad (5)$$

where  $(1/t_{1/2})_o$  is the pre-exponential factor. Figure 4 shows a plot of  $1/t_{1/2}$  versus  $1/T\Delta T f$  where  $t_{1/2}$  is calculated at peak crystallization temperature ( $T$ ) for all cooling scans. The slope of the straight line for Figure 4 is associated with nucleation related parameter  $K_g$ .<sup>[13, 15]</sup> From Figure 4 it is seen that the line depicting pure PET has the least

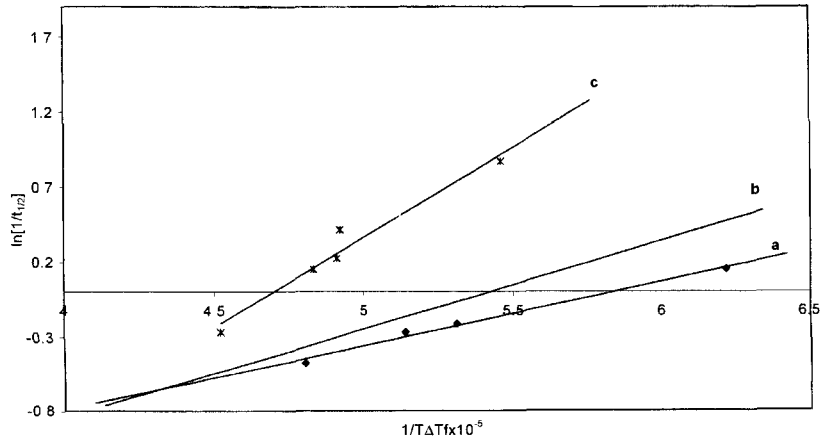


FIGURE 4 Plot of  $\ln\{1/t_{1/2}\}$  against  $1/T\Delta T f$  for PET blends: (a) pure PET, (b) 50% PS blend, (c) 50% nylon 6 blend.

slope, whereas PET/50% PS blend has a higher slope than pure PET, and PET/50% nylon 6 blend has the greatest slope. Therefore, the maximum nucleation is facilitated in PET/50% nylon 6 blends followed by PET/50% PS blends, and then PET homopolymer.

## CONCLUSIONS

- (i) The apparent activation energy and nucleation facilitation for the samples studied are in the order: PET < PET/50% PS < PET/nylon 6. Whereas crystallization half time is in the reverse order in the temperature range of 480–486 K.
- (ii) The Avrami exponent ( $n$ ) for PET homopolymer and PET/50% PS and PET/50% nylon 6 blend is found to vary between 2 to 3 ( $2 < n < 3$ ), which signify random nucleation with two-dimensional diffusion-controlled growth.

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