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Crystallization Characteristics Of Pet/TiO$_2$ Nanocomposites

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ABSTRACT

A series of poly(ethylene terephthalate) (PET)/TiO$_2$ nanocomposites were prepared via in situ polymerization from dimethyl terephthalate and ethylene glycol/TiO$_2$ suspension. DSC measurements indicate that the crystallization temperature from the melt moves to high temperature compared to neat PET while the value of melting point as well as the crystallinity first increases and then decreases slightly with increasing TiO$_2$ content. The results derived from the isothermal crystallization study demonstrate that the incorporated TiO$_2$ nano particles play the role of nucleus and generally enhance the crystallization rate of PET/TiO$_2$ nanocomposites. The crystal growth in nanocomposites mainly conforms to the two-dimensional form with heterogeneous nucleation. WAXD analysis explains that the crystal lattice in PET is generally not affected by the presence of TiO$_2$.
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INTRODUCTION

It is well known that the polymer/inorganic particles nanocomposites have attracted more and more attention for this decade, since they exhibit improved mechanical and thermal properties[1-3], gas permeability[4] and fire retardance[5] compared to the pristine polymer. These enhanced properties are related to the extremely high surface area of nano-particle which facilitates creating a great amount of interphase in a composite. The presence of the interphase may change the intermolecular interaction of the matrix[6]. But, the above stated positive effects could be achieved based on adequately dispersing the inorganic nano-

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particles or clay particles within the polymer matrix. Only in this way, the disadvantages generated by the heterogeneity of conventional particles filled composites can be avoided. Rong et al.[7-8] demonstrated for epoxy/TiO_2 nanocomposites that the impact property and wear performance significantly depends on the dispersion state and the micro structural homogeneity of the fillers.

It's very interesting how the nano inorganic particles influence the crystallization behavior. There are some reports concerned the effects of clay on the crystallization behavior of PET/clay nanocomposites[9-10]. The addition of clay reduces the induction time of crystallization and increase the crystallization rate. The PET/montmorillonite clay nanocomposite was synthesized via in situ polymerization by Wan et al[10]. They found the clay could greatly increase the crystallization rate of PET. The Avrami exponent of PET/clay is smaller than that of PET, which is consistent with the observation of the rodlike crystallites in PET/clay and spherulitic growth in during the early stage of crystallization. Hu and Lesser[11] studied the crystallization characteristics of bisphenol-A polycarbonate (PC) and PC/clay nanocomposites in the presence of supercritical carbon dioxide ($SCCO_2$). It was found that in the absence of $SCCO_2$, nano scale clay itself does not change the crystallization behavior of PC; in the presence of $SCCO_2$ clay appears to be an efficient nucleating agent and enhances the crystallization of PC.

In the previous work, L.Hao et al.[12] have reported the preparation of PET/TiO_2 nano composites via in situ polymerization. In this work, the effect of TiO_2 on the crystallization behavior and kinetics of PET matrix was investigated by conducting differential scanning calorimetric (DSC) and wide angle X-ray scattering (WAXS).

EXPERIMENTAL

Materials

The nano TiO_2 dispersed in water (STS-02, TiO_2%=30%, pH =1.5) with an average primary particle size of 7nm was supplied by Ishihara Sangyo Co. Ltd. Ethylene glycol (EG) was purchased from Kanto Kagaku Co.Ltd. Dimethyl terephthalate (DMT) is commercially available and not purified before use.

Preparation of nanocomposites

PET/TiO_2 nanocomposites were synthesized starting from DMT and EG/TiO_2 suspension (EG/DMT=2.2 mol ratio). The syntheses were carried out according to the usual trans-esterification technique as described elsewhere[12]. The samples obtained have intrinsic viscosity from 0.55dL/g (PET nanocomposites with TiO_2 weight content of 0.5% and 1 wt%) to 0.50dL/g (PET nanocomposites with 2 wt%). The neat PET of intrinsic viscosity of 0.56dL/g was used for comparison.

Characterization of the neat PET and PET/TiO_2 nanocomposites

The crystalline and melting temperatures were detected by Modulated DSC 2910 (TA Instruments, USA).The weighed samples were encapsulated in aluminum pans and heated up to 280°C, kept at this temperature for 3 min to remove any thermal history, and then cooled to room temperature (the cooling scanning). Finally, they were reheated again up to 280°C (the heating scanning). The rate of heating and cooling is 10°C/min.

Isothermal crystallization analysis was performed on Perkin Elmer pyres-1 system (USA.) under nitrogen atmosphere. Samples were first heated from 40°C to 280°C at a heating rate of 20°C/min and kept at 280°C for 5 min in order to destroy any nuclei that might act as seed crystals, then cooled to predetermined temperature (198°C, 203°C, 208°C and 213°C) at a rapid cooling rate of 100°C/min, and remained isothermal until the crystallization was completed. The exothermic enthalpy in isothermal crystallization with crystallization time was recorded.

WAXS analysis was performed on BRUKER-AXC08 X-ray diffractometer with Cu Kα radiation (λ=0.1542nm; 40kV; 40mA). Both neat PET and PET/TiO_2 samples were annealed at 130°C for 3 hours before measurement
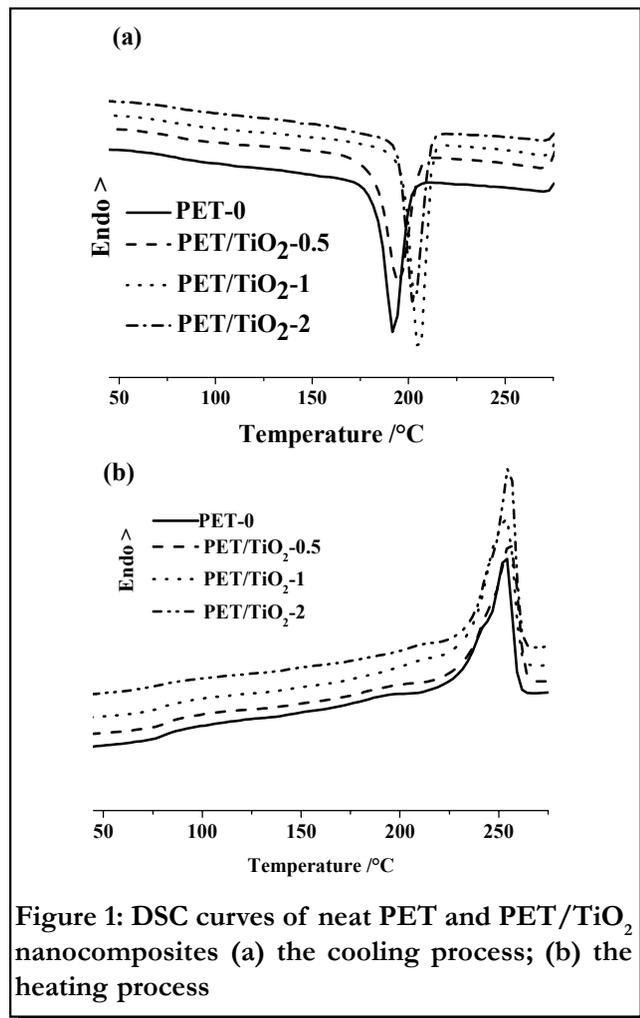
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Figure 1: DSC curves of neat PET and PET/TiO$_2$ nanocomposites (a) the cooling process; (b) the heating process

become narrower was also found. The current results are coincident with the previous observations. PET/BaSO$_4$ composites exhibited higher crystallization temperature (T_c=203°C) from the melt during cooling than neat PET (T_c=191°C)[13], and the crystallization peak width (ΔT_c) for the PET/BaSO$_4$ composites is narrower by 6-10°C than that of neat PET. The PET/SiO$_2$ composites also showed the same trend in the change of crystallization temperature[14]. So that nano sized particles act as a nucleating agent on PET crystallization during cooling from the melt has been accepted to explain this observation[10], which will be described in detail in the following section.

Figure1(b) depicts the heating runs of neat PET and PET/TiO$_2$ nanocomposites. It was found that the melting point (T_m) increases and then decreases slightly with the increasing of TiO$_2$ content. The T_m value is related to the perfection of spherulites. Usually, there are two major effects acting simultaneously when the inorganic particles filled polymer undergoes crystallization. One is the decrease in mobility of the chain segments, and the other is the heterogeneous nucleation. The heterogeneous nucleation would accelerate the deposition of polymer molecules and the crystalline spherulites formed at a higher temperature tend to be larger and possess less defects, leading to a higher T_m in subsequent heating. In another hand, it is expected that the nano particles could more or less hinder the motion of the polymer chain segments, and in turn impart the smaller and more defects spherulites to the resulting nanocomposites. And therefore, T_m would be lower in consequence. It appears that a small amount (0.5 wt%) of nano TiO$_2$ would provide enough sites for nucleation and accelerating the deposition of poly-

RESULTS AND DISCUSSIONS

DSC analysis of PET/TiO$_2$ nanocomposites

Figure1(a) shows the cooling curves of neat PET and PET/TiO$_2$ nanocomposites. The crystallization onset (T_{on}) and peak (T_c) shift to higher temperatures for nanocomposites compared to those of neat PET. And that the crystallization exothermic peaks

TABLE 1: Summary of DSC data

Samples	Melting			Crystallization			
	T_m/°C	ΔH_m/J•g^{-1}	X_c /%	T_{on}/°C	T_c/°C	ΔH_c/J•g^{-1}	ΔT^*/°C
PET-0	254	-36.57	34.5	209	190	41.41	64
PET/TiO$_2$-0.5	257	-39.9	37.6	210	195	42.95	62
PET/TiO$_2$-1	254	-42.53	40.1	214	204	47.59	50
PET/TiO$_2$-2	252	-34.92	33.0	217	202	45.34	50

$^*\Delta T = T_m - T_c$

mer molecules and thus in turn, both T_c and T_m increase. With increasing of TiO_2 content, the hindrance to the motion of polymer chain segments would play a reverse effect and T_m tends to decrease. In order to gain an insight into the effects on the degree of crystallinity (X_c) of PET, the normalized X_c values of the sample were determined using the following equation:

$$X_c = (\Delta H_m / \Delta H_m^0) \times 100$$

where ΔH^o_m is the melting enthalpy of 100% crystalline PET ($\Delta H^o_m = 105.97 J/g$) and ΔH_m is the melting enthalpy of the samples during the second heating process. For the sample of PET/TiO_2-1, X_c is about 40%, higher than that of PET-0 (34.5%). However, with the content of TiO_2 increasing, X_c intends to decease, suggesting that high TiO_2 content will inhibit the mobility of chain segments and thus in turn, the growth of crystals.

Isothermal crystallization kinetics

The experimental crystallization exothermic traces at predetermined temperature are given in figure 2. The exothermic peaks at the same temperature firstly become sharp with the incremental addition of TiO_2. The dependence of crystallization transformation X(t) on crystallization time for neat PET and PET/TiO_2 composites at 213°C was plotted in figure 3. It is revealed clearly that the crystallization rate of PET/TiO_2 is generally enhanced by the incorporation of TiO_2 into PET. And the change of the half time of crystallization ($t_{1/2}$) with respect of TiO_2 content was given in figure 4. Meanwhile, it is also noticed that some induction time is needed for neat PET to crystallize; otherwise almost no induction time is required for PET/TiO_2 composites to crystallize. The presence of TiO_2 as predetermined nucleation agent may be responsible to this difference.

To understand the effect of TiO_2 on the crystallization behavior of PET further, the isothermal crystallization kinetics was studied according to the Avrami equation,

$$1 - X(t) = \exp(-k(T)t^n) \qquad (1)$$

where X(t) is the crystallization transformation developed after time t, k(T) is the crystallization rate
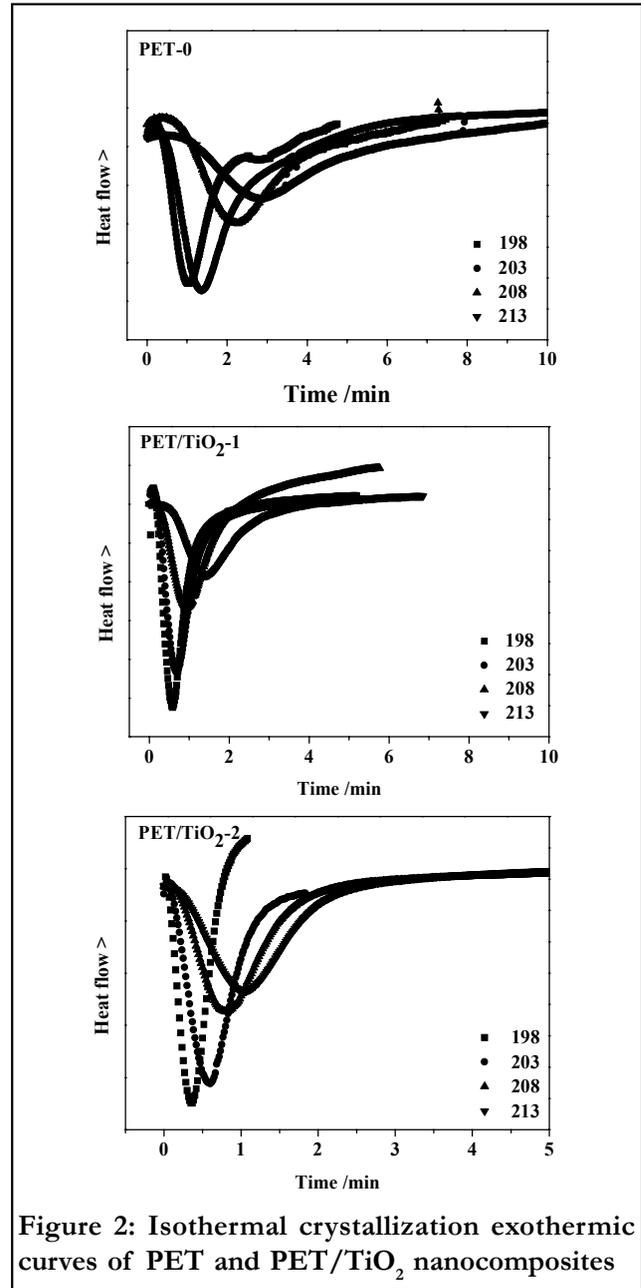

Figure 2: Isothermal crystallization exothermic curves of PET and PET/TiO₂ nanocomposites

constant associated with the rate of nucleation and growth and n is the Avrami exponent, the values of which depends on the primary nucleation and growth geometry of the crystalline entities. The values of n and k(T) are usually obtained from the double logarithmic form of above equation,

$$\ln[-\ln(1 - X(t))] = \ln k(T) + n \ln(t) \qquad (2)$$

Here, X(t) could be related to the ratio of exothermic enthalpy ($\Delta H_c(t)$) at time t over totally exothermic enthalpy ($\Delta H_c(\infty)$) after infinite time period. While crystallization develops at a predetermined temperature T, there is
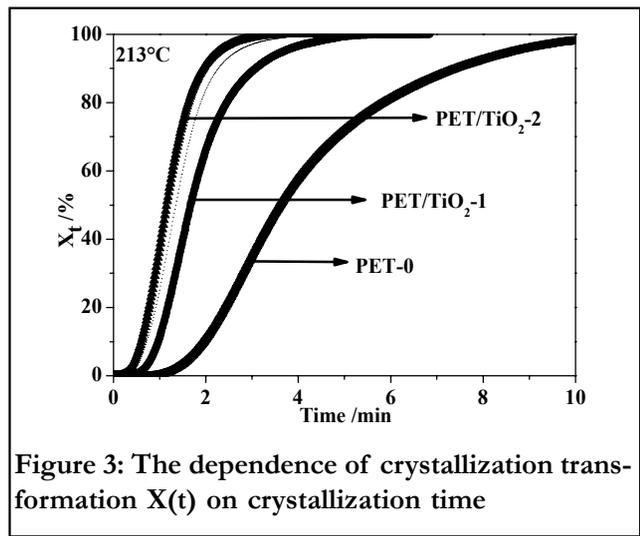
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Figure 3: The dependence of crystallization transformation X(t) on crystallization time
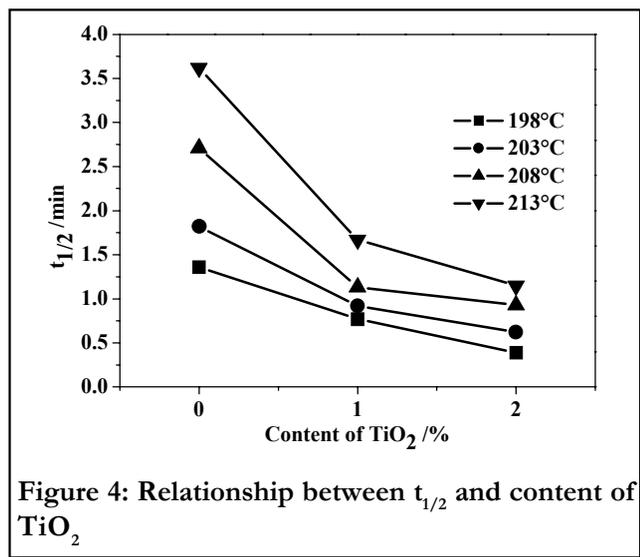

Figure 4: Relationship between $t_{1/2}$ and content of TiO₂

$$X(t) = \frac{\Delta H_c(t)}{\Delta H_c(\infty)} = \frac{\int_0^t \frac{dH_c(t)}{dt} dt}{\int_0^\infty \frac{dH_c(t)}{dt} dt} \qquad (3)$$

Plots of ln[-ln(1-X_t)] versus ln t for neat PET and nanocomposites are shown in figure 5. The Avrami exponent n and the overall kinetic rate constant k, obtained by the fitting of straight lines to the initial parts of the curves, are given in TABLE 2. The half time of crystallization can be calculated by the following equations.

$$t_{1/2} = (\ln 2 / k)^{1/n} \qquad (4)$$

From TABLE 2, it is very clear that k values increase significantly with incremental TiO₂ addition. The half time ($t_{1/2}$) of crystallization decreases with
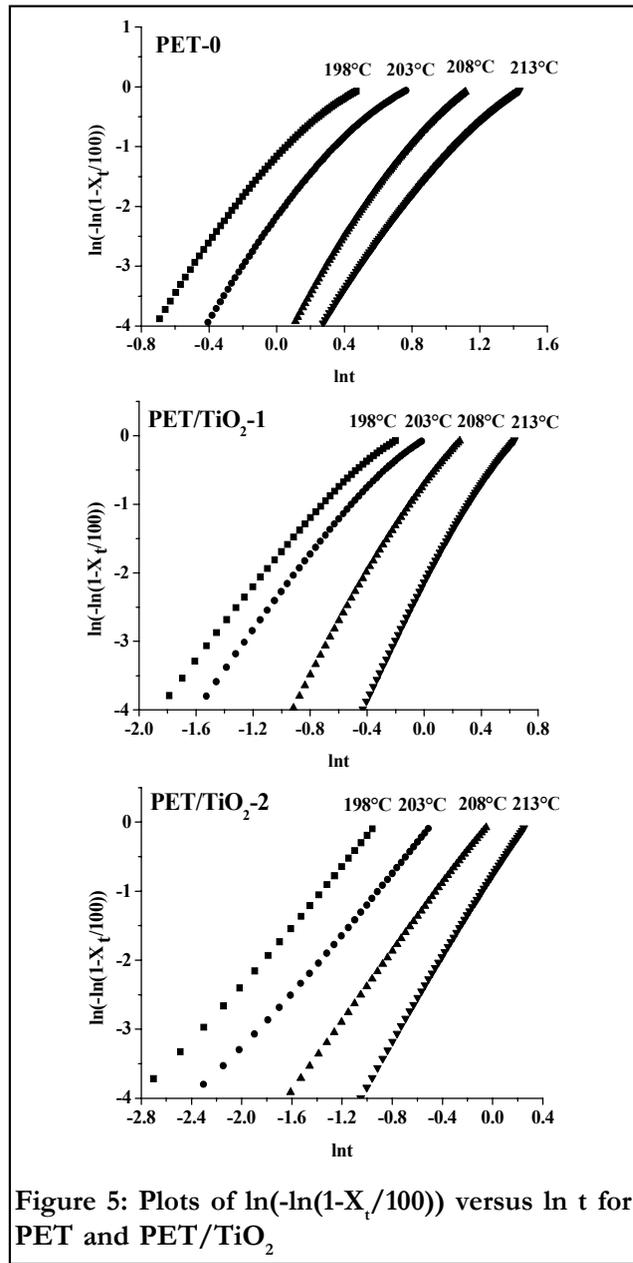

Figure 5: Plots of ln(-ln(1-X_t/100)) versus ln t for PET and PET/TiO₂

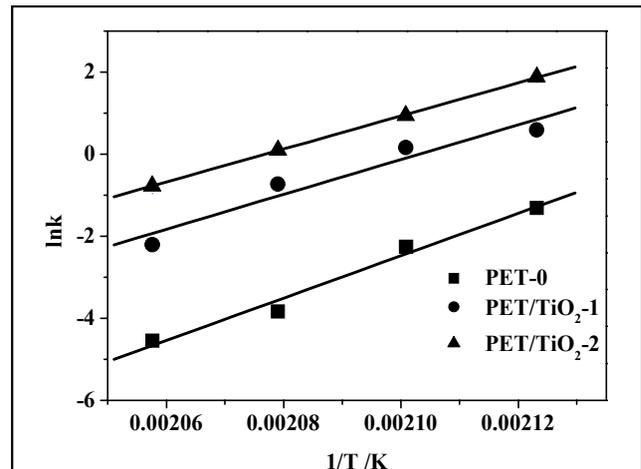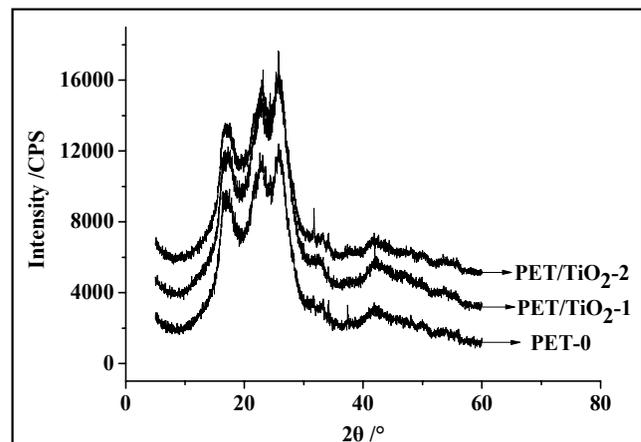increase of TiO₂ content in the same way, which is consistent with that in figure 4.

It is well know that the Avrami exponent n describes the nucleating mechanism and growing geometry dimensions of crystallization. As shown in TABLE 2, the Avrami exponent n is about 3 at all the investigated temperatures, whereas the n value for PET/TiO₂ composites shows much smaller, and becomes lower with more addition of TiO₂ at the same crystallization temperature. So it is reasonable to deduce that the growth of crystallization for neat PET is three-dimensional (spherulitic) with homogeneous nucleation mechanism, because no any ad-

TABLE 2: Avrami rate parameters for neat PET and PET nanocomposites

Sample	Temperature/°C	n	k	$t_{1/2}$
PET-0	198	3.19	0.27	1.33
	203	3.22	0.10	1.79
	208	3.50	0.022	2.63
	213	3.27	0.011	3.49
PET/TiO$_2$-1	198	2.34	1.80	0.66
	203	2.45	1.16	0.80
	208	3.29	0.48	1.11
	213	3.67	0.11	1.64
PET/TiO$_2$-2	198	2.10	6.55	0.34
	203	2.11	2.56	0.54
	208	2.48	1.10	0.82
	213	2.99	0.46	1.14

Figure 6: Change of activation energy of the overall crystallization with crystallization temperatures

Figue 7: WAXS diffraction of neat PET and PET/TiO$_2$ composites

ditives as a nucleation agent was added, whereas the crystal growth in PET/TiO$_2$ composites mainly is two-dimensional, probably in rodlike or platelike form with heterogeneous nucleation mechanism, i.e. nano TiO$_2$ as a nucleating agent. The similar result was usually obtained in other nano-particle filled PET composites. Tong Wan et al.[10] found the Avrami exponent n of PET/clay is about 2.0-2.3, and n of PET is 3.1-3.3 when they studied isothermal crystallization behavior of PET/clay nanocomposites at the temperature 210-230°C. Both nano TiO$_2$ and nano clay could act as substrates to initialize crystallization of PET, just like 'in situ' crystallization, at the same time, most of the crystallites in nano-particle filled PET composites cannot complete their three-dimensional growth in all directions. Many growing crystal branches will be terminated because of the presence of clay or TiO$_2$ in their growth paths. The more content of nano particle, the more serious hindrance to crystal growth is. This may be why n value decreases with increasing TiO$_2$ content (shown in TABLE 2). Of course, there are still some crystallites which could grow in three-dimensions in PET/TiO$_2$ composites, especially when the addition of TiO$_2$ is low.

The temperature dependence of crystallization rate constant k is compared by means of the activation energy, which can be obtained from the slopes of the plots of lnk versus (1/T) according to the Arrhenius equation

$$k = A_0 \exp(-E_a / RT) \tag{5}$$

Figure 6 shows that the activation energy of the nanocomposites is smaller than that of the neat PET at the same crystallization temperature. Furthermore, the rate constant difference between neat PET and PET/TiO$_2$ nanocomposites becomes large at high temperature. Thus it can be said that it is nanometer TiO$_2$ that act as nucleation agents to initianize crystallization which is more effective at higher crystallization temperature, because homogeneous nucleation is more difficult at high temperature

Crystalline structure measured by WAXS

To investigate the influence of nano TiO$_2$ particles on the crystalline structure and crystalline structure, WAXS measurements on both neat PET and

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the PET/TiO$_2$ nanocomposites were performed. The results are shown in figure 7. The diffraction peak positions of nanocomposites are identical to those of neat PET, indicating that the crystal lattice in PET is generally not affected by the presence of TiO$_2$.

CONCLUSIONS

A series of PET/TiO$_2$ nanocomposites were prepared via in situ polymerization. The crystallization temperature from the melt moved to high temperature with increasing TiO$_2$ content. The value of melting point as well as crystallinity first increases and then decreases with the incremental addition of TiO$_2$. It appears that the crystallization rate as well as crystallinity reaches the maximum when 1 wt% TiO$_2$ is involved. The isothermal crystallization study on both neat PET and PET/TiO$_2$ nanocomposites explained that the addition of TiO$_2$ could significantly enhance the rate of crystallization of PET. The crystallization of PET in the presence of TiO$_2$ progressed mainly in two-dimension growth with nano TiO$_2$ as a nucleating agent, while neat PET crystallized in three-dimension growth with homogenous nucleation mechanism. The crystal lattice in nanocomposites does not change obviously.

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