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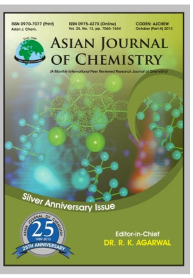

Effects of Multi Amide Compound Nucleating Agent on Non-isothermal Crystallization of Semi-aromatic Polyamide 6T/6

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The influence of multi amide compound nucleating agent TMC-328 on the nonisothermal crystallization behaviour of the semi-aromatic polyamide 6T/6(PA6T/6) is investigated. It is observed that the crystallization peak temperature (T_p) of PA6T/6-TMC328 is marginally higher than neat PA6T/6 at various cooling rates. Furthermore, the half-time for crystallization ($t_{1/2}$) decreased with in TMC-328, implying the nucleating role of TMC-328. The nonisothermal crystallization data is analyzed using Avrami and Combined Ozawa-Avrami method. The validity of kinetic models on the nonisothermal crystallization process of PA6T/6-TMC328 is described. The activation energy for nonisothermal crystallization of neat PA6T/6 and PA6T/6s with contents of TMC-328 based on Kissinger method is evaluated.

Key Words: Polyamide 6T/6, Nucleating agent, Crystallization, Non-isothermal, Kinetic.

INTRODUCTION

Semi-aromatic polyamides have been widely used in many industrial and commercial applications, by virtue of their excellent characteristics such as good thermal stability, chemical resistance, low creep and high modulus. Some of these polymers are considered as high-performance materials[1-6].

Generally, the crystallization rate of semi-crystalline polymers can be enhanced by accelerating the nucleation. The additives called nucleating agents (NAs) play an important role in the acceleration of heterogeneous nucleation[7]. Nucleating agents can induce high crystallization temperature and degree of crystallinity (X_c) of polymer in the cooling process. Thus, the addition of nucleating agents can improve the process sability, productivity in molding-injection processing, thermal properties, mechanical strengths and moduli of semi-crystalline polymers. Many kinds of nucleating agents have been developed and their effects on crystallization kinetics and physical properties have been investigated for a series of semi-crystalline polymers. but it should be noted that there are no literature data about the application of nucleating agents in semi-aromatic polyamide 6T/6.

TMC-328 is a multi amide compound nucleating agents product which is announced by Shanxi Institute of Chemical Industry, China (SPICI). TMC-328 is a novel efficient nucleating agents for PLA, PET, PBT and polyolefin[8].

In this study, we investigated the non-isothermal crystallization behaviour of PA6T/6 by introducing nucleating agents TMC-328.

EXPERIMENTAL

The polyamide 6T/6 (PA6T/6) used in the study was prepared in our laboratory(η = 2.56 Pa.s, T_m = 281.4 ºC), prepared as described in reference[9]. TMC-328 was supplied by SPICI with melting point over 350 ºC.

All materials were dried in an oven at 100 ºC for 12 h. The PA6T/6 composites containing different TMC-328 nucleating agent contents (from 0-5 %) were prepared *via* a melt compounding method using an torque rheometer RM-200A with a screw speed of 50 rpm. In this process, the temperature profile was 300 ºC and the blending time was 8 min.

Thermal analysis was performed in a DSC 200 F3 (NETZSCH, German) differential scanning calorimeter. The instrument was calibrated using high purity indium and zinc standards. For isothermal crystallization, the samples were melted at 320 ºC for 3 min to eliminate the previous thermal history and then were cooled at a constant rate to 50 ºC. The preset cooling rates were 5, 10, 15, 20 and 30 ºC/min, respectively.

RESULTS AND DISCUSSION

Non-isothermal melt crystallization behaviours: The effects of multi amide compound nucleobase on the melt crystallization of PA6T/6 were investigated by DSC analysis. Fig. 1 shows the DSC curves of non-isothermal melt-crystallization for the neat PA6T/6 and PA6T/6 composites containing different TMC-328 nucleating agent contents. The non-isothermal crystallization parameters such as the onset temperature of crystallization (T_o), the end temperature of crystallization (T_c) and the exothermic peak temperature of crystallization (T_p) are determined from these curves and the results are shown in Table-1.

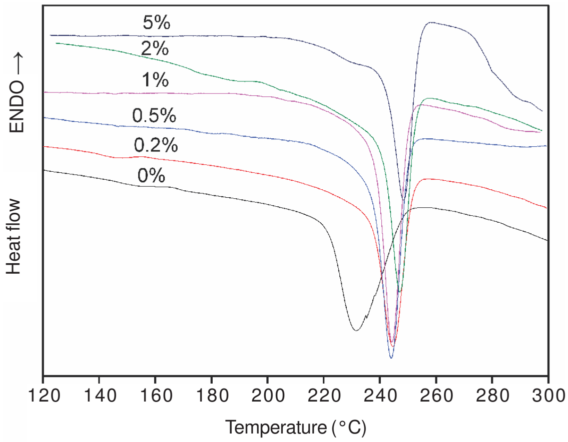

Fig. 1. DSC cooling curves of neat PA6T/6 and PA6T/6 composites at a cooling rate of 10 °C/min

It is found that the introduction of TMC-328 in PA6T/6 leads to a significant increase in T_o, T_c and T_p. For example, at the cooling rate of 10 °C/min, crystallization peak temperature for neat PA6T/6 is 231.6°C, while for PA6T/6 composites containing 0.2wt% TMC-328, it is 244.7°C. This implies that the TMC-328 acts as efficient nucleating agent to increasing the rate of crystallization of PA6T/6.

Non-isothermal crystallization kinetics: Fig. 2 shows typical DSC curves of heat flow as a function of temperature at different cooling rates for neat PA6T/6 and PA6T/6-0.2 wt % TMC-328. The non-isothermal crystallization parameters T_o, T_c and T_p have been determined from these curves and the results have been shown in Table-2. It is clear that as the rate of cooling increases, all the parameters namely T_o, T_c and T_p shift to lower temperatures.

The relative degree of crystallinity X_t is required for the analysis of crystallization kinetics and the X_t as a function of temperature is defined as:

$$X_t = \frac{\int_{T_0}^{T} (dH/dT)dT}{\int_{T_0}^{T_\infty} (dH/dT)dT} \qquad (1)$$

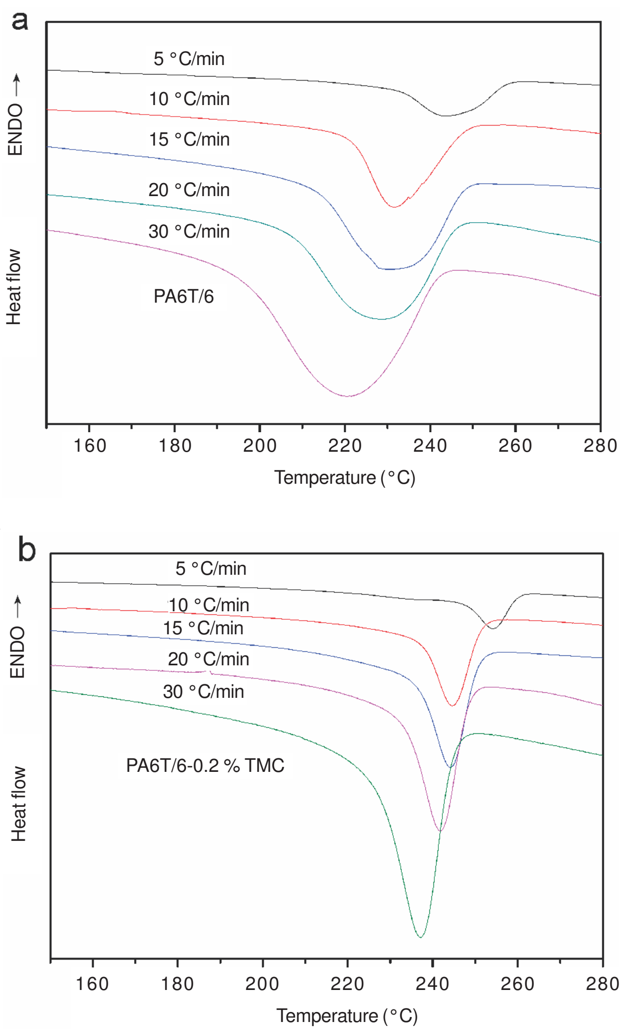

Fig. 2. DSC curves of PA6T/6 (a) and PA6T/6-TMC (0.2 wt %) composites (b)

TABLE-2
NONISOTHERMAL CRYSTALLIZATION KINETIC DATA OF PA6T/6 AND NUCLEATED PA6T/6

Samples	Φ (°C) min^{-1}	n	Z_c	$t_{1/2}$ (min)	Tp (°C)
PA6T/6	5	2.3	0.52	3.33	243.8
	10	2.5	0.84	1.98	231.6
	15	2.2	0.94	1.31	230.5
	20	2.0	0.97	1.03	228.7
	30	2.0	1.00	0.79	220.7
PA6T/6-0.2wt% TMC	5	2.7	0.63	1.99	254.2
	10	3.4	0.90	1.19	244.7
	15	3.3	1.00	0.86	244.1
	20	3.4	1.04	0.66	241.9
	30	3.3	1.06	0.51	237.3

TABLE-1
THERMAL PARAMETERS OF PA6T/6 AND PA6T/6 COMPOSITES ATTAINED IN NONISOTHERMAL MELT-CRYSTALLIZATION PROCESSES

Sample	T_p (°C)	T_o (°C)	T_c (°C)	ΔT_c (°C)	ΔH (J g^{-1})
PA6T/6	231.6	247.6	222.9	18.5	23.56
PA6T/6 TMC (0.2 %)	244.7	251.1	237.7	10.8	24.84
PA6T/6 TMC (0.5 %)	243.9	249.7	237.7	9.4	27.79
PA6T/6 TMC (1 %)	244.3	249.7	238.5	8.6	28.19
PA6T/6 TMC (2 %)	247.1	252.5	241.3	9.2	25.42
PA6T/6 TMC (5 %)	248.4	253.8	242.8	9.8	23.97

where T_0 and T_∞ are the onset and end temperatures of crystallization, respectively and H is the enthalpy of crystallization. Using the following equation, t = $(T_0 - T)/\varphi$ (where T is the temperature at crystallization time t and φ is the cooling rate), the abscissa of temperature could be transformed into a timescale. Fig. 3 shows the relative degree of crystallinity, X_t, as a function of crystallization temperature T and crystallization time t for PA6T/6 and PA6T/6-0.2 wt % TMC-328 at various cooling rates. The higher the cooling rate is, the shorter the crystallization time span is. The half time of non-isothermal crystallization ($t_{1/2}$), which is defined as the time taken the crystallinity of the sample reaches the value of 50 % of the relative crystallinity, was estimated from the Xc-t curves (Fig. 3). The results are listed in Table-2.

Avrami analysis of non-isothermal crystallization: The modified Avrami equation is widely used to describe the polymer non-isothermal crystallization[10].

$$1 - X_t = \exp(-Z_t t^n) \tag{2}$$

where, X_t is the relative crystallinity at the crystallization time t. The 'n' is Avrami exponent, which is a mechanism constant depending on type of nucleation and growth process. According to original assumptions of the theory, the value of the Avrami exponent 'n' should be an integer ranging from 1-4. The Z_t is the Avrami rate constant for crystallization involving nucleation and growth parameters. The double logarithm of the eqn. 2 gives the following relation:

$$\ln[\ln(1 - X_t)] = \ln Z_t + n \ln t \tag{3}$$

Since the process is non-isothermal, Jeziorny[11] suggested that the rate parameter Z_t should be corrected for the influence of cooling rate Φ of the polymer. Assuming to be constant or approximately constant, the final form of the parameter characterizing the kinetics of non-isothermal crystallization was given as follows:

$$\log Z_c = \frac{\log Z_t}{\Phi} \tag{4}$$

Fig. 4 presents the plot of ln[-ln $(1-X_t)$] *versus* ln t of neat PA6T/6 and PA6T/6-0.2 wt % TMC-328 with preferable linear relation. The values of n and Z_t can be obtained by the fitting of the linear slopes and the intercepts of the lines, respectively. The rate constant of crystallization, Z_c, can be obtained by eqn. 4. The values of n and Z_c are listed in Table-2.

The values of Avrami exponent 'n' for PA6T/6 and PA6T/6-0.2 wt % TMC-328 range from 2.0-2.5 and 2.7-3.4, respectively. From the data it is clear that the values of n for PA6T/6-0.2 wt % TMC-328 are all higher than PA6T/6. which implies that presence of TMC-328 in PA6T/6 drastically modied the crystallization mechanism of composites. This may be due to the predominant nucleation activity of the TMC-328 molecules in PA6T/6.

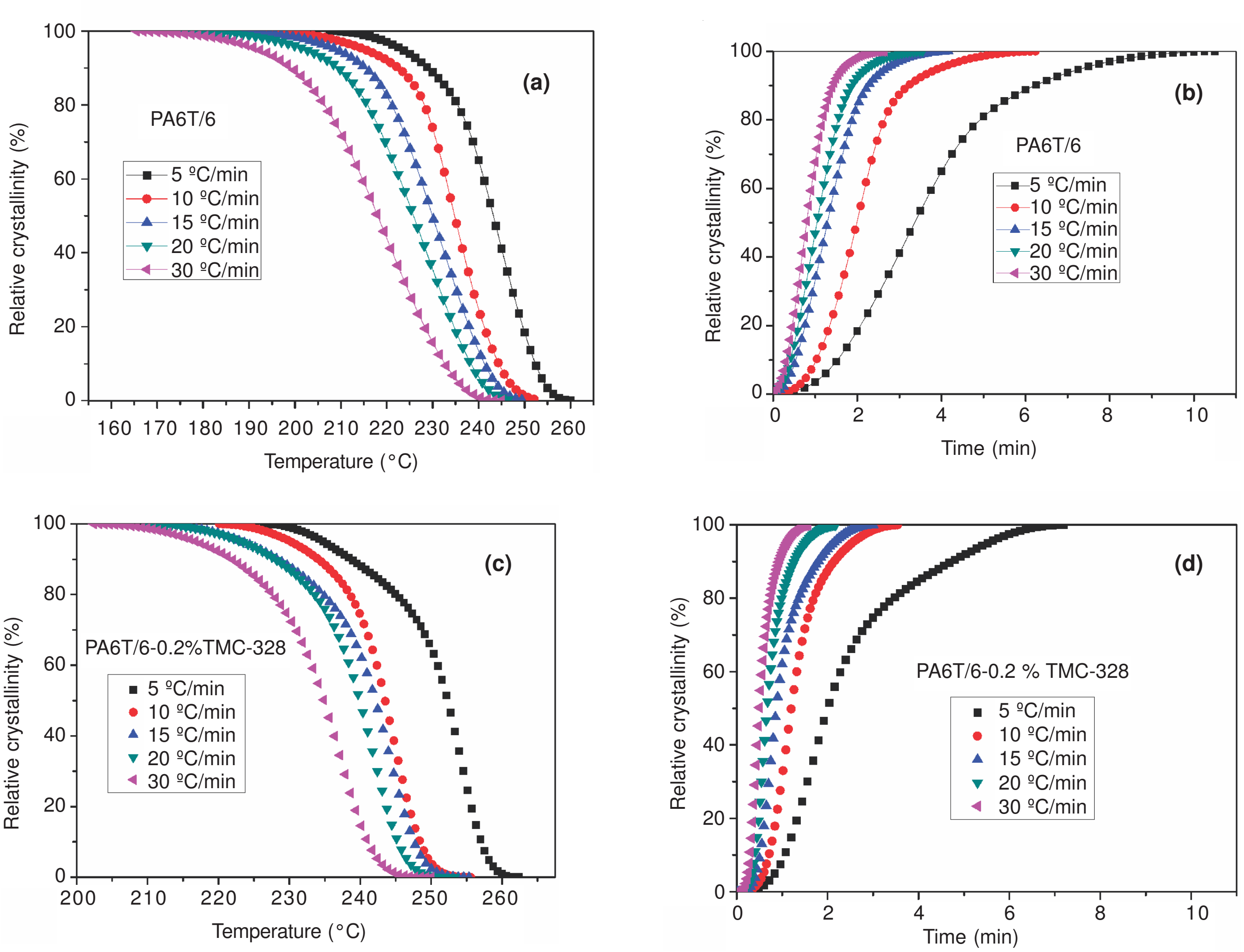

Fig. 3. Plots of X_t *versus* T or t for crystallization of samples at different cooling rates

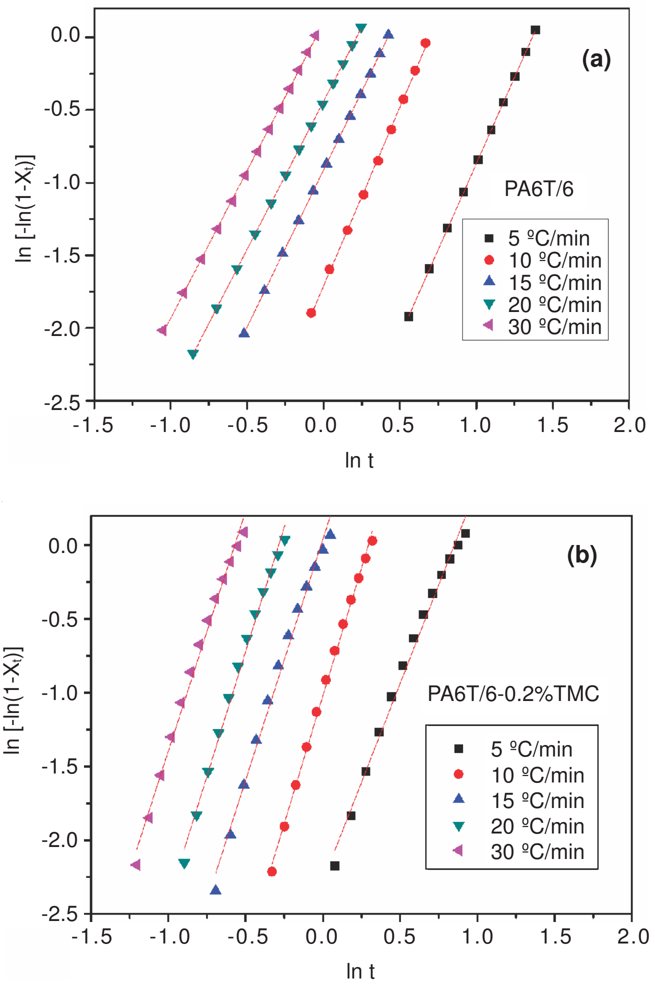

Fig. 4. Plot of ln [-ln(1-X_t)] *versus* lnt for non-isothermal crystallization of neat PA6T/6 (a) and PA6T/6-0.2 wt % TMC-328 (b)

Table-2 showed that the crystallization peak temperature T_p and the value of $t_{1/2}$ decreases and the Z_c increases with increasing the cooling rate for all the samples. The lower $t_{1/2}$ and higher Z_c for PA6T/6 filled with TMC-328 are attributed to the presence of the heterogeneous nucleation of TMC-328. The $t_{1/2}$ is lower and the T_p and Z_c are higher for nucleated PA6T/6 compared to that of pure PA6T/6 under the same cooling rate. It means that the crystallization rate of PA6T/6 nucleated with TMC-328 nucleating agent is higher than that of PA6T/6.

Combined Ozawa-Avrami approach: The Mo method is the combination of Avrami and Ozawa equations[12] and the simplified formula is:

$$\log\phi = \log F(T) - \alpha \log t \qquad (5)$$

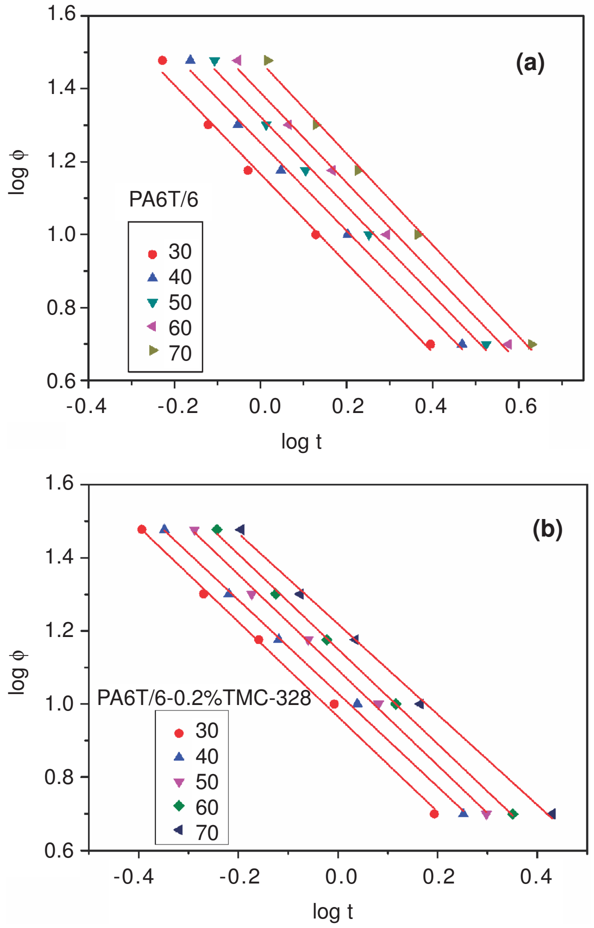

Fig. 5. log ϕ *versus* log t for neat PA6T/6 (a) and PA6T/6-0.2 wt % TMC-5 composites (b) from the combined Avrami and Ozawa equation

TABLE-3
VALUES OF F(T) AND α *VERSUS*.
DEGREE OF CRYSTALLINITY FOR PA6T/6
AND NUCLEATED PA6T/6 WITH TMC

X(t) (%)		30	40	50	60	70
PA6T/6	F(T)	14.62	17.86	21.03	24.43	29.71
	α	1.22	1.21	1.22	1.23	1.25
PA6T/6-0.2 wt % TMC	F(T)	9.23	10.69	12.39	14.16	16.56
	α	1.29	1.28	1.30	1.29	1.24

where F(T)refers to the value of the cooling rate chosen at a unit crystallization time at which the system has a certain degree of crystallinity. According to eqn. 5, straight lines with intercept of log F(T) and slope α can be obtained by plotting log ϕ *versus* log t (Fig. 5). Data of log F(T) are collected in Table-3. It can be seen that the value increases with increase in relative crystallinity for all polymers studied. It indicated that a higher cooling rate should be required to obtain a higher relative crystallinity in the same crystallization time. At a given relative crystallinity, the value of of PA6T/6 nucleated with TMC-328 is lower than that of PA6T/6. Such results are similar to those obtained in the analysis on $t_{1/2}$ and Z_c. These results indicate that the crystallization rate of PA6T/6 nucleated with TMC-328 is higher than that of PA6T/6.

Crystallization activation energy: Detailed kinetic analysis can give more information about the thermal transition inside the polymer materials. The Kissinger method[13] is one of the most commonly used methods, through which the activation energy of the non-isothermal crystallization process can be easily obtained. The basic form of the Kissinger equation is shown in eqn. 5, where Φ is the cooling rate, T_p is the peak temperature, ΔE is the activation energy and R is the gas constant.

$$\frac{d[\ln(\Phi/T_p{}^2)]}{d[\ln(1/T_p)]} = -\frac{\Delta E}{RT_P} \qquad (5)$$

Then the activation energy can be calculated from the slopes of plots of ln ($\Phi/T_p{}^2$) *versus* 1/T_p (Fig. 6) by using the relation, ΔE = R × slope. The ΔE values of neat PA6T/6 and

PA6T/6 filled with 0.2 wt % TMC-328 nucleating agent are -178.5 and -250.8 kJ mol^{-1}, respectively. ΔE is negative due to exothermic nature of the transition from melt to crystalline state and negative activation energy values also imply that crystallization mechanisms are accelerated by decreasing the temperatures. Negative activation energy values have been reported for non-isothermal crystallization of PBT[12] and PET[14] composite systems. From the data it is obvious that the presence of TMC-328 causes significant changes in the value of activation energy in the PA6T/6. It is also found that ΔE value of PA6T/6-TMC-328 is lower than PA6T/6 which refers to TMC-328 act as nucleating agents by lowering the crystallization activation energy. It is apparent that TMC-328 can accelerate the crystallization of PA6T/6.

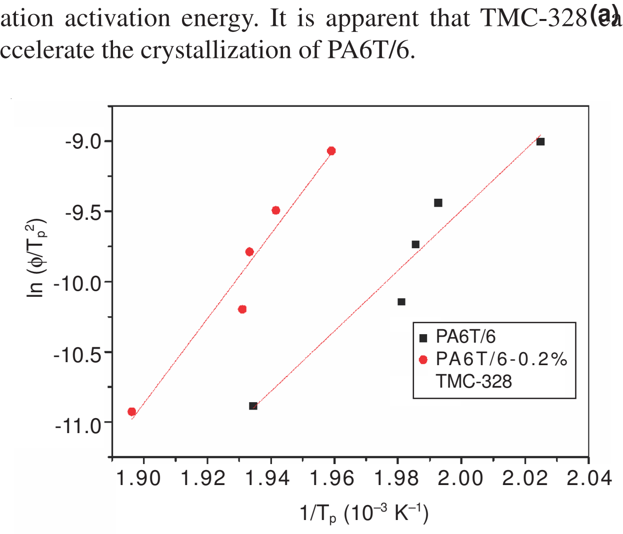

Fig. 6. Plots of ln(ϕ/T_p^2) *vs*. 1/T_p for samples crystallized non-isothermal

Conclusion

Non-isothermal crystallization kinetics and crystallization activation energies of PA6T/6 nucleated with multi amide compound nucleating Agent TMC-328 are compared with those of neat PA6T/6. The crystallization temperature of PA6T/6 increases and the crystal form of PA6T/6 is influenced when TMC-328 is added as nucleating agent, the crystallization rate of PA6T/6 nucleated with TMC-328 nucleating agent is higher than that of pure PA6T/6 . The crystallization activation energy of PA6T/6 nucleated with TMC-328 is lower than that of neat PA6T/6. The TMC-328 nucleating agent exhibits higher efficiency for PA6T/6 crystallization.

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