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ISOTHERMAL CRYSTALLIZATION BEHAVIOUR OF POLY(ETHER-ETHER-KETONE) (PEEK) AND ITS CARBON FIBER COMPOSITE

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ABSTRACT

The crystallization behaviour of PEEK and its carbon fiber composite, APC-2, has been studied by DSC. The mean Avrami exponents, $\bar{n}$, of PEEK are 5.0 and 3.9 for the crystallization processes from the melt and from the rubbery amorphous state respectively, while the $\bar{n}$ of APC-2 are 3.5 and 2.3 correspondingly The activation energies of PEEK are 532.0 KJ/mol for crystallization from the melt and 531.7 KJ/mol for crystallization from rubbery state, while the activation energies of APC-2 are 444.2 and 432.5 KJ/mol respectively.

INTRODUCTION

Poly(ether-ether-ketone), PEEK, is a new kind of high performance engineering thermalplastic with good processability, mechanical properties and excellent solvent resistance(1,2). Due to the excellent properties, it is possible to take the place of the thermoset epoxy resin used as a matrix of high performance composites. This paper deals with the isothermal crystallization of PEEK and its carbon fiber composite, APC-2, by means of differential scanning calorimeter (DSC).

EXPERIMENTAL

Samples used in this study are PEEK and APC-2 obtained from Imperial Chemical Industry (ICI). PEEK sample is light yellow transparent amorphous film with thickness of 0.1 mm. APC-2 composite is based on a continuous unidirectional carbon fibers embedded in PEEK matrix. The content of carbon fiber

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measured by thermogravimetry (TG) is 66 wt%, near to the value of 68 % reported in literature$^{(3)}$.

The enthalpy changes of samples during the crystallization process were determined by a Perkin-Elmer DSC-2C. For the isothermal crystallization at higher temperature range from the melt, the crystallizing temperatures (T_c) were chosen at the range of 300°C to 325°C. It was necessary to first heat the samples to 400°C (the equilibrium melting temperature of PEEK is 395°C$^{(4)}$) for 2 minutes in order to eliminate thermal history of the sample and then rapidly cool to the given crystallizing temperature. While for the isothermal crystallization from the rubbery state, the crystallizing temperatures (T_c) were chosen at the range of 155°C to 165°C. As for obtaining the amorphous sample at the temperature lower than 170°C the cooling rate should be faster than 1000°C/min$^{(3)}$, it is necessary first to heat the sample to 400°C for 2 minutes and then quench into ice water in order to get the perfect amorphous sample and subsequently heat to the given crystallizing temperature rapidly.

The relative degree of crystallinity at time t, $X_c(t)/X_c(\infty)$, can be obtained from:

$$X_c(t)/X_c(\infty) = \int_0^t \frac{dH(t)}{dt}dt \Big/ \int_0^\infty \frac{dH(t)}{dt}dt \qquad (1)$$

where $X_c(t)$ is the crystallinity at time t; $X_c(\infty)$ is the maximum crystallinity at crystallizing temperature T_c; $\frac{dH(t)}{dt}$ is the heat flow rate. $X_c(t)$ was found from:

$$X_c(t) = \int_0^t \frac{dH(t)}{dt}dt \Big/ (1 - \varphi_{cf})\,\Delta H_f \qquad (2)$$

where φ_{cf} is the weight percentage of carbon fiber content. For APC-2, $\varphi_{cf} = 0.66$, while for PEEK only, $\varphi_{cf} = 0$. ΔH_f is the heat of fusion for perfect crystal determined from the area under a DSC endotherm. For perfect crystal PEEK, $\Delta H = 130$ J/g$^{(4)}$.

RESULTS AND DISCUSSION

In Table 1, a number of t_{max} data under different T_c crystallizations from melt and from rubbery state of samples are listed. Also listed are the relative crystallinity at time t_{max},

Table 1. t_{max}, $X_c(\infty)$ and $X_c(t_{max})/X_c(\infty)$ of PEEK and APC-2 under different T_c.

sample	T_c (°C)	t_{max} (min)	$X_c(\infty)$ (%)	$X_c(t_{max})/X_c(\infty)$
PEEK	314	12.8	34	0.39
	312	7.6	34	0.39
	308	3.8	34	0.39
	306	3.3	34	0.40
APC-2	323	15.4	45	0.49
	319	7.7	40	0.47
	317	5.7	40	0.43
	315	4.7	40	0.43
	313	2.5	40	0.43
PEEK	165	1.7	15	0.45
	164	2.1	16	0.43
	162	4.7	15	0.49
	160	8.6	13	0.47
APC-2	164	1.5	18	0.41
	163	2.0	18	0.47
	162	2.9	18	0.41
	161	3.6	16	0.42
	157	11.0	15	0.47

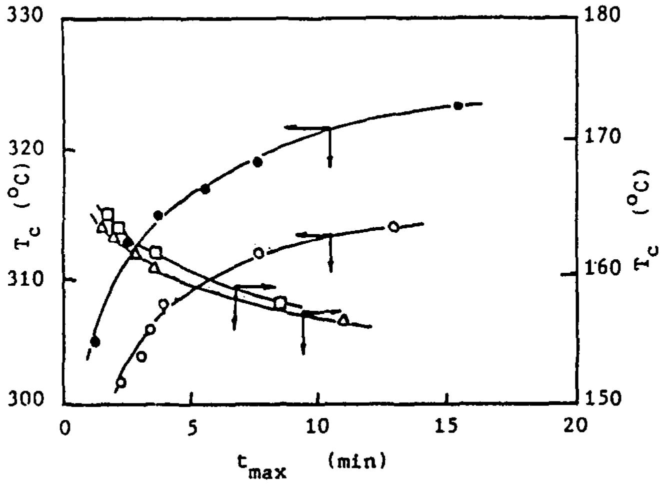

Fig. 1. Plot of T_c vs. t_{max} during isothermal crystallization from melt and from rubbery state of PEEK and APC-2 samples.
(○) and (□): PEEK;
(●) and (△): APC-2.

$X_c(t_{max})/X_c(\infty)$, and the ultimate crystallinity $X_c(\infty)$, where t_{max} is the time at which the rate of crystallizing exotherm reached the maximum. As for PEEK, the relative degree of crystallinities under the high temperature crystallization are smaller than those under the lower temperature crystallizations, and are also smaller than the relative crystallinities of APC-2 under both conditions of crystallization. The absolute crystallinity, $X_c(\infty)$, of simple PEEK is always smaller than that of APC-2 under the same T_c, no matter which crystallizing condition is taken. Moreover, the difference of $X_c(\infty)$ values appears more marked under the conditions of high temperature crystallization. Yet we can see that the t_{max} value of PEEK at a certain T_c is slightly larger than that of APC-2. The relationship between T_c and t_{max} during isothermal crystallization for PEEK and APC-2 has been plotted in Figure 1. It is obvious that whether the crystallization was conducted from the melt or from the rubbery state at a specified T_c, both made the t_{max} value of APC-2 smaller than that of PEEK, especially during the crystallization from the melt. The above experimental results illustrate: 1. The surface of carbon fibers had the effect on promoting crystallization of PEEK matrix further; 2. The surface of carbon fibers showed the effect on increasing the crystallizing rate of PEEK matrix.

The kinetic relation between the development of the relative crystallinity with time can be analyzed by using the Avrami equation:

$$X_c(t)/X_c(\infty) = 1 - \exp(-kt^n) \qquad (3)$$

where n is Avrami exponent whose value depends on the mechanism of nucleation and the form of crystal growth, and k is a constant of crystallizing rate whose value depends on the rate of crystal growth(5,6). Plots of $\log(-\ln[1-X_c(t)/X_c(\infty)])$ versus log t are shown in Figure 2. As seen, the curves of $\log(-\ln[1-X_c(t)/X_c(\infty)])$ vs. log t are basically linear at the initial stage and depart from linearity at longer times. This phenomenon is concerned with secondary crystallization of PEEK. From Table 1 the mean values of the absolute crystallinity at time t_{max}, $X_c(t_{max})$, of PEEK for both the melt crystallization and the rubbery crystallization are 13.3 % and 6.8 % respectively, while the mean values of $X_c(t_{max})$ of APC-2 are 18.6 % and 7.6 %

respectively. It is apparent that about half as much material crystallizes at low remperatures. In addition, the proportion of uncrystallized PEEK sample, at t_{max} time, is larger than that of APC-2 sample. Further crystallization leads the plots departing from linearity at longer times. Fitting the initial linear portion of curves of $\log(-\ln[1-X_c^*(t)/X_c(\infty)])$ vs. log t allows us to determine n and k from equation (3). The values are listed in Table 2. The n values of PEEK are obviously higher than those of APC-2 indicates that the surface of carbon fiber in APC-2 composite has changed the crystallization behaviour of PEEK matrix. Within the range of $300^oC < T_c < 325^oC$, the mean value of Avrami exponent, $\bar{n}$, of PEEK is 5.0, while $\bar{n}$ of APC-2 is 3.5. And within the range of $155^oC < T_c < 170^oC$, $\bar{n}$ are 3.9 and 2.3 for PEEK and APC-2 respectively.

As a result of $\bar{n}$ = 5.0 for PEEK under the melt crystallization we consider the crystal structure of PEEK as solid sheaf(5). The larger value of $\bar{n}$ is caused by the presence of nucleating agent in ICI's PEEK which was reported in the literature(8). Under the cold crystallization of PEEK, the mean value of Avrami exponent, $\bar{n}$, reduced to 3.9. This indicates that the effect of nucleating agent on the cold crystallization is weaker than that on the melt crystallization. The reason is that PEEK is kept in a high degree of supercooled state under cold crystallization, and part of amorphous PEEK crystallize by means of homogeneous nucleation, thus the effect of nucleating agent appears weaker and the crystal structure becomes more complicated.

APC-2 consists of 66 wt% of carbon fiber which is able to induce crystallization and to change the crystal structure of PEEK matrix(3,7). In the present experiment, we obtained the $\bar{n}$ values of APC-2 for the melt crystallization and cold crystallization are 3.5 and 2.3 respectively; and the crystal structure is truncated sphere(5). These indicate that the carbon fiber may fully change the crystal structure of PEEK matrix and may make the original nucleating agent has no effect upon the crystallization.

Providing that crystallization is thermal activation process, we can write the approximant as follows(8):

$$k^{\frac{1}{n}} = k_o \exp(-\Delta E/RT) \qquad (4)$$

Table 2. The values of n and k for PEEK and APC-2 obtained from Avrami equation.

sample	T_c (°C)	n	k (s^{-n})
PEEK	314	5.2	5.2×10^{-16}
	312	5.1	1.1×10^{-14}
	308	4.9	1.4×10^{-12}
	306	4.7	8.0×10^{-12}
APC-2	323	3.3	1.4×10^{-10}
	319	3.7	9.4×10^{-11}
	317	3.4	1.4×10^{-9}
	315	3.4	3.4×10^{-8}
	313	3.0	8.6×10^{-7}
PEEK	165	3.4	7.5×10^{-8}
	164	3.4	3.4×10^{-8}
	162	3.9	1.5×10^{-10}
	160	4.7	9.9×10^{-14}
APC-2	164	2.2	2.5×10^{-5}
	163	2.2	1.4×10^{-5}
	162	2.7	7.2×10^{-7}
	161	2.4	1.8×10^{-6}
	157	2.1	8.8×10^{-7}

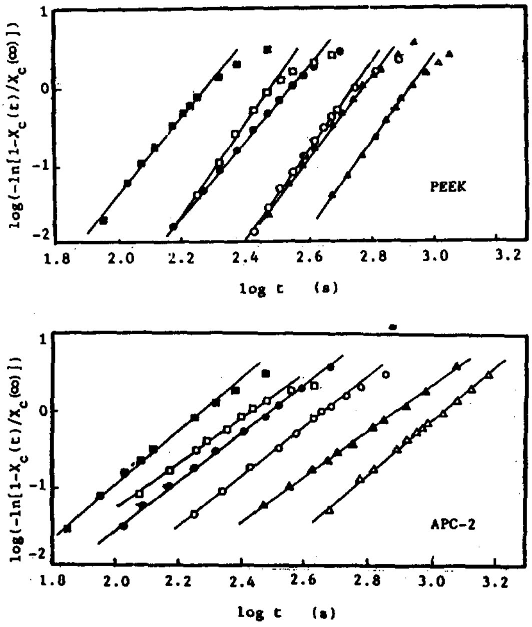

Fig. 2. Plot of $\log(-\ln[1-X_c(t)/X_c(\infty)])$ vs. log t for isothermal crystallization of PEEK and APC-2 samples.
PEEK: (△): 314°C; (○): 312°C; (□): 308°C; (▲): 160°C; (●): 162°C; (■): 164°C.
APC-2: (△): 323°C; (○): 317°C; (□): 313°C; (▲): 157°C; (●): 161°C; (■): 163°C.

where k_0 is a temperature independent preexponential, ΔE is the activation energy, R is the gas constant. From data listed in Table 2, the activation energies of crystallization of PEEK and APC-2 can be calculated. The activation energies of PEEK and APC-2 are 532.0 and 444.2 KJ/mol respectively for the melt crystallization, while the activation energies are 531.7 and 432.5 KJ/mol for the cold crystallization. In view of this, the crystallization is easier for PEEK matrix in APC-2 than that for single PEEK. These results are consistent with the above experimental results.

REFERENCES

(1) T. E. Attwood, P. C. Dawson, J. L. Freeman, L. R. J. Hay, J. B. Ross and P. A. Staniland, Polymer, 1981, 22, 109.
(2) M. T. Bishop, F. E. Karasz, P. S. Russo and K. H. Langley, Macromolecules, 1985, 18, 86.
(3) D. J. Blundell, J. M. Chalmers, M. W. Mackenie and W. F. Gaskin, SAMPE Q., 1985, 16, 22.
(4) D. J. Blundell and B. N. Osborn, Polymer, 1983, 24, 953
(5) B. Wunderlich, " Macromolecular Physics ", Academic Press, New York, 1976, Vol. 2.
(6) J. M. Schultz, " Polymeric Materials Science ", Prentice -Hall, New York, 1981.
(7) Youngchul Lee and S. R. Porter, Polym. Eng. Sci., 1986, 26, 633.
(8) Peggy Cebe and Sun-Don Hong, Polymer, 1986, 27, 1183.