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Crystallization kinetics of J-1 polymer under different thermal treatments

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A *bis*-para-amino cyclohexylmethane (PACM)-based polyamide homopolymer (J-1 polymer produced by Du Pont), utilized as a matrix for composites, was subjected to different thermal treatments in order to investigate its crystallization thermodynamics and crystallization kinetics. Various J-1 samples, quenched, annealed from the glassy state, isothermally crystallized from the melt and slowly cooled, were studied by differential scanning calorimetry (DSC). A thermodynamic melting temperature of 352.6 °C was determined from a Hoffman–Weeks diagram of polymer samples annealed at different temperatures between the glass transition and melting temperature. By using DSC isothermal crystallization data from the melt, the existence of two crystallization regimes, already found in a previous investigation, was confirmed, and a transition temperature between the two regimes, equal to 262.2 °C was determined, in good agreement with 260.5 °C, obtained by depolarized light measurements, reported elsewhere. Moreover, the ratio between the crystallization kinetics factor of two crystallization regimes is 1.87, very close to the value of 2 predicted by the Hoffman theory. Crystallization of samples from the melt, at different cooling rates, was also performed. The Arrhenius plot of data indicated that the crystallization process proceeds with two distinct activation energies (589 and 244 kJ mol^{-1}), below or above a cooling rate of 2.67 °C min^{-1}, corresponding to a temperature of 253.9 °C. This result is in good agreement with the two crystallization regimes reported above.

1. Introduction

The thermal treatment imposed on a polymer, both thermoplastic and thermoset, plays a significant role in determining its final properties. In semicrystalline polymers, different thermal histories may produce different crystalline morphologies and variations in the degree of crystallinity. For these polymers, property characterization and optimization by thermal analysis is essential, and because their thermal behaviour is reflected in the melting and recrystallization enthalpies during cooling or heating cycles, differential scanning calorimetry is considered an effective tool [1, 2].

J-1 polymer is a semicrystalline polyamide homopolymer, poly[(*bis*-4,4′-dicyclohexylmethane)*n*-dodecanediamide], which has been demonstrated as a matrix for high-performance composites by a variety of manufacture processes [3–13]. Owing to the chain rigidity induced by the cyclohexyl units and the amide bond to the intermolecular hydrogen bonding, J-1 polymer exhibits a relatively high glass transition temperature (149 °C) [11] and different melting points according to the thermal history [3, 9], and to potential crystalline polymorphism, attributed to the presence of CH_2 groups [8, 13]. It was reported [13] that six different types of J-1 polymer spherulites can grow simultaneously during solvent evaporation, involving three different crystallographic unit cells. All of these structures differ from that reported for quenched-annealed samples [8].

This paper reports part of a wider research on the effect of crystallinity on the physical and mechanical properties of J-1 polymer and its carbon fibre composites [14–16]. In a previous work, high-modulus carbon fibre was shown to act as a nucleant agent able to develop a transcrystalline layer on its surface. The effects of such a layer on the fibre–matrix adhesion and on the carbon-fibre reinforced plastics (CFRP) mechanical properties were investigated [16]. The bulk crystallization kinetics and the transcrystalline layer growth rate were evaluated by an optical microscope investigation. A double crystalline morphology was identified [15].

In the present work, attention was focused on the matrix crystallization processes and their kinetics under different thermal conditions, and on identification of the corresponding morphologies. In particular, the transition between crystallization regimes II and

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III was investigated by differential thermal analysis and compared with previous observations based on depolarized light intensity, recorded by hot-stage microscopy follow-up of the crystallization process [16].

2. Experimental procedure

2.1. Materials

J-1 polymer, supplied by Du Pont as thin sheets, was melted, quenched in ice–water and carefully dried before thermal treatments and analysis. The as-received J-1 polymer showed a glass transition temperature, T_g, of 149 °C, a melting point at around 285 °C, and a crystallinity content of about 15%. After melting and quenching, the resulting polymer crystallinity was less than 10%.

2.2. Thermal treatments and analyses

The different thermal treatments were performed with polymer samples of about 50 mg in the differential scanning calorimeter (Mettler DSC 30) under nitrogen, flushed at $100\,\mathrm{ml\,min^{-1}}$.

A range of treatment cycles comprising specific combinations of heating, melting annealing and cooling was employed as follows. (i) Annealing: the polymer was heated at $10\,^\circ\mathrm{C\,min^{-1}}$ up to 300 °C at which it was retained for 5 min, followed by quenching to room temperature at $-100\,^\circ\mathrm{C\,min^{-1}}$. Annealing of the quenched polymer was performed by an isothermal treatment at selected annealing temperatures, T_a, between the glass transition temperature (149 °C) and the melting point of the as-received J-1 polymer, i.e. in the range 150–285 °C. (ii) Isothermal crystallization: molten polymer samples were rapidly cooled to a selected crystallization temperature, T_c, in the range 240–280 °C, where they were retained for a crystallization period ranging from 30–120 min, followed by quenching to room temperature. (iii) Slow cooling crystallization: molten polymer samples were cooled to the glass transition temperature, at different rates ranging from -0.05 to $-50\,^\circ\mathrm{C\,min^{-1}}$, followed by fast cooling to room temperature.

Each thermal treatment was characterized by a subsequent DSC scan from 0–340 °C at a heating rate of $10\,^\circ\mathrm{C\,min^{-1}}$, and the data were analysed by a Mettler TA72 programme. The value of $150\,\mathrm{J\,g^{-1}}$ was taken as the melting enthalpy of the 100% crystalline J-1 polymer [9].

3. Results and discussion

This paper reports a continuation of our study of bulk and interface crystallization processes of J-1 polymer/carbon fibre composites [16]. Whereas the previous study focused on isothermal crystallization, this one investigates other thermal treatments as well. Moreover, the kinetics analysis that was previously based on measurements of the depolarized light passing through the samples during isothermal treatments, is now augmented with DSC-based measurements.

3.1. Annealing treatments

The data from the annealing treatment experiments were utilized to determine the thermodynamic melting point, T_{m0}, by the Hoffman–Weeks diagram [17]. The procedure is based on the polymer crystallization theory that argues that the experimental melting temperature depends on the dimensions of spherulites and on their degree of perfection. As the thermodynamic value corresponds to a perfect crystal of infinite dimensions, the experimental one, corresponding to an imperfect structure, is lower. Moreover, because the annealing treatment improves the crystalline quality of the polymer, the experimental melting point is shifted to higher temperatures as the annealing temperature is raised. Based on these arguments it is possible to determine T_{m0} by plotting the experimental melting temperature of the crystalline phase against the annealing temperature at which it developed (the Hoffman–Weeks diagram). The intersection between the best-fit line and the diagonal $T_m = T_a$ is taken as thermodynamic melting point. For the J-1 polymer, where more than one crystalline structure could be observed [9, 16], the procedure is still applicable as long as the highest melting point is considered [18]. Annealing treatments of the quenched polymer in the range 150–250 °C, gave a melting point very close to the melting temperature of the as-received J-1 polymer, from which a thermodynamic melting temperature of 288.4 °C was calculated. The temperature was considered in a previous paper [16] discussing the J-1 polymer crystallization according to the Hoffman theory. However, longer times and higher temperature annealing treatments produced J-1 polymer samples having much higher melting temperature and crystallinity content. In fact, as shown in Fig. 1, the melting temperature and crystallinity of J-1 samples annealed at 280 °C for 100 h, are 300 °C and 34%, respectively. Fig. 2 presents the Hoffman–Weeks diagram for J-1 polymer samples annealed between 150 and 285 °C, from which a thermodynamic melting temperature, T_{m0}, of 352.6 °C, was derived.

3.2. Isothermal crystallization

The kinetics of isothermal crystallization can provide important information on structure and morphology,

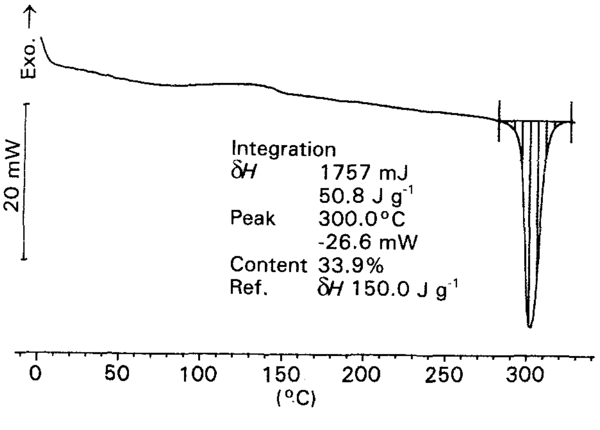

Figure 1 DSC thermogram of J-1 polymer annealed at 280 °C for 100 h.

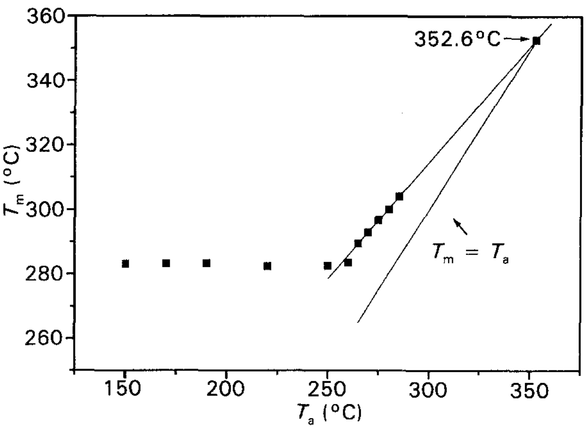

Figure 2 The Hoffmann–Week diagram. T_m of the higher melting points for J-1 polymer as function of the annealing temperature in the range 150–285 °C.

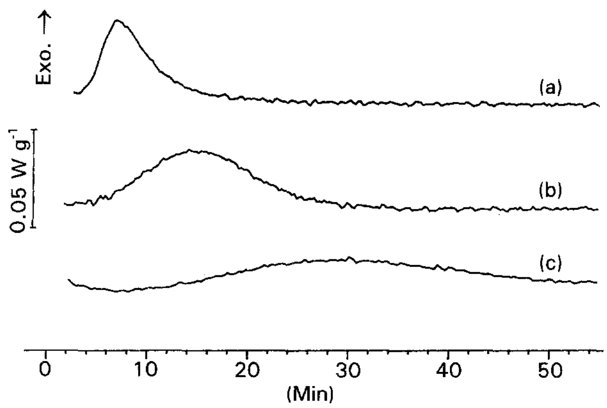

Figure 3 Isothermal crystallization of J-1 polymer performed in the DSC at (a) 257.5 °C, (b) 265 °C and (c) 270 °C.

which develop in a thermoplastic polymer as function of processing conditions (time and temperature), as, for example, reported for PEEK and PEEK/carbon fibre composites [19–22].

The molten J-1 polymer was quenched to different crystallization temperature, T_c, and then isothermally treated at these temperatures. At temperatures lower than 240 °C the crystallization is too fast to be registered by DSC, and at temperatures higher than 280 °C the process is so slow that the signal is comparable with the noise of the apparatus. Fig. 3 presents a set of thermograms of isothermal crystallization experiments at selected crystallization temperatures. The time, t_c, required to reach one-half of the final crystallinity amount [23], defines the bulk crystallization kinetics factor, $K(T_c) = 1/t_c$. In the literature, which refers to the same [16] or to other polymers [24], crystallization kinetics was characterized by a bulk crystallization kinetics factor $K(T_{1/2}) = 1/t_{1/2}$, where $t_{1/2}$, corresponds to the mean value between the initial and final intensities of depolarized light which passes through the sample during crystallization. Fig. 4 presents a plot of $K(T_c)$ as function of T_c, where two regimes are clearly evident. The regime transition occurs at 260.3 °C delineated by the intersection of the two straight lines best fitting the experimental points. This result agrees well with the value of 257.6 °C, based on the depolarized light measurements, reported earlier [16]. In Hoffman's modified equation [25], the crystallization kinetics factor, $K(T_c)$, can be correlated to the nucleation constant, K_g, by the relation

$$\log K(T_c) + U^*/2.303R(T_c - T_0) = \log K_0 - K_g/2.303T_c(T_{m0} - T_c) \qquad (1)$$

where U^* is the constant of the activation energy of transport of molecules to the crystal surface (6280 J mol^{-1}); R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T_0 is the temperature at which any viscous flow is assumed to be negligible ($T_0 = T_g - 30$ °C = 119 °C) [26], K_g is the characteristic nucleation constant (expressed in K^2 units where K is Kelvin) for each crystallization regime, K_0 is a pre-exponential factor (a priori unknown expressed in s^{-1} units). Equation 1 can be used to determine the regime transition temperature by using the experimental $K(T_c)$ values to plot its left hand side against $[2.303\, T_c\,(T_{m0} - T_c)]^{-1}$. A value of $T_{m0} = 352.6$ °C, as determined in Fig. 2, was used in the calculation. The resulting plot shown in Fig. 5 confirms the existence of two crystallization regimes which, according to Hoffman's theory, are identified as regimes II and III for the higher and lower temperature ranges, respectively. The regime transition temperature occurs at 262.2 °C, compared with that of 260.5 °C reported earlier [16]. The respective nucleation constants in the two regimes are $K_{gII} = 5.68 \times 10^{-5}$ K^2 and $K_{gIII} = 10.65 \times 10^{-5}$ K^2, and the respective pre-exponential factors are $K_{0II} = 3.01 \times 10^4$ s^{-1} and $K_{0III} = 8.95 \times 10^9$ s^{-1}. These values are significantly different from those reported previously [16], as a result of the fact that whereas in the previous calculation a T_{m0} value of 288.4 °C was assumed, this one uses a more accurate value of $T_{m0} = 352.6$ °C. The ratio $K_{gIII}/K_{gII} = 1.87$ (compared with the previous 5.1) is therefore more accurate and falls much closer to the value of 2 predicted by Hoffman's theory. It is interesting to note that if the value of $T_{m0} = 352.6$ °C is used with the $K(t_{1/2}) = 1/t_{1/2}$ data taken from the depolarized light experiment [16], a ratio of $K_{gIII}/K_{gII} = 1.56$ and a transition temperature of 261.4 °C will result. Hence,

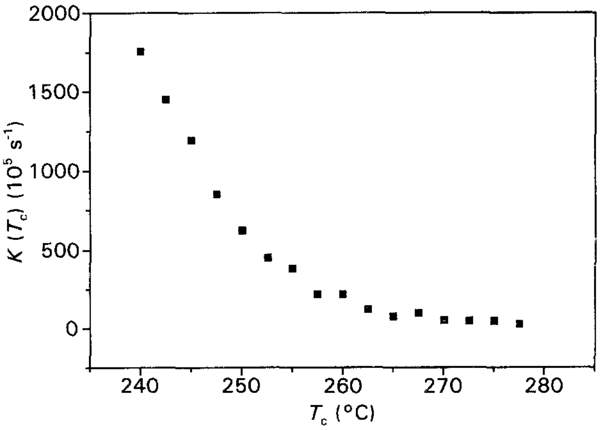

Figure 4 Bulk crystallization factor, $K(T_c) = 1/t_c$, as function of isothermal crystallization temperature, T_c.

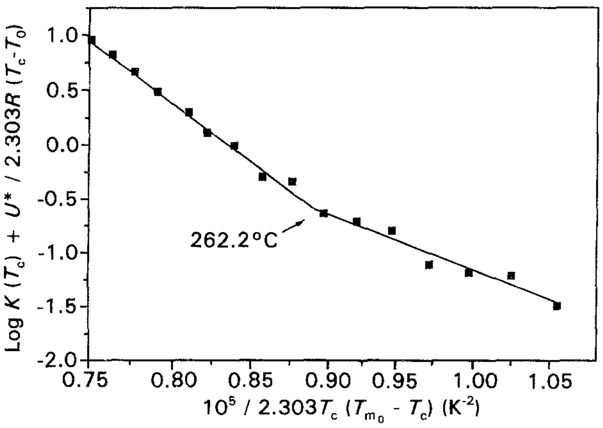

Figure 5 Calculated values of the first member of Hoffmann's modified equation, log $K(T_c) + U^*/2.303R(T_c - T_0)$, as function of $1/2.303T_c(T_{m0} - T_c)$, expressed in K^{-2}; $K(T_c)$ is expressed in s^{-1}.

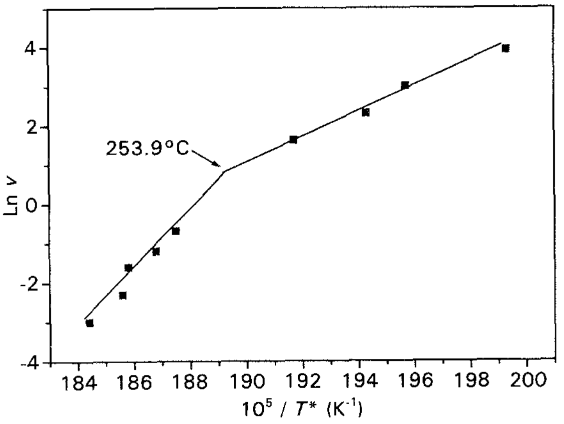

Figure 6 Cooling rate, v ($°C\,min^{-1}$) versus temperature of the highest crystallization rate, T^* (K), reported in the Arrhenius form.

both techniques give results consistent with the theoretical value, but the DSC method appeared to be more accurate.

3.3. Constant rate cooling

Assuming that the temperature of the highest crystallization rate, T^*, defined as the temperature of the maximum of the crystallization peak in each cooling thermogram, is related to the cooling rate, v, by an Arrhenius-type equation, the activation energy of crystallization, E_{act}, can be worked out for each crystallization from Equation 2 [27], as follows

$$\ln v = \ln v_0 - (E_{act}c/R)1/T^* \qquad (2)$$

where v_0 is a pre-exponential factor (a priori unknown expressed in $°C\,min^{-1}$) and $c = 1.052$ is the constant reported in the literature [27]. Fig. 6 presents a plot of the experimental values of ln v against $1/T^*$, the inverse of the temperature of highest crystallization rate. It is evident that the experimental data can be best fitted with two lines, whose slope express the activation energies according to Equation 2. The two lines are indicative of two processes, with the respective activation energies of 589 and $244\,kJ\,mol^{-1}$, for cooling rates slower and faster than $2.67\,°C\,min^{-1}$. These activation energies differ slightly from those reported for PEEK in APC-2 composites [27]. The two processes, characterized by two activation energies, correspond to crystallization regimes II and III, respectively, with a calculated regime transition point, corresponding to a cooling rate of $2.67\,°C\,min^{-1}$, equal to 253.9 °C, slightly lower than the values obtained from isothermal crystallization.

4. Conclusions

The existence of two different crystallization regimes, already observed in J-1 polymer by measurements of depolarized light intensities, has been confirmed in differential scanning calorimetry experiments both in isothermal and dynamic crystallization treatments. A well-defined thermodynamic melting temperature, equal to 352.6 °C, has been determined, by using the Hoffman–Weeks approach on J-1 polymer samples annealed at different temperatures. A transition between the two crystallization regimes found, equal to 262.2 °C, has been determined in good agreement with the corresponding data obtained by the reported depolarized light measurements [16] (i.e. 261.4 °C) if the thermodynamic melting temperature value reported above is used.

Crystallizations performed on samples cooled from the melt at different cooling rates, indicate an Arrhenius dependence of the cooling rate on the temperature of the highest crystallization rate, with two different activation energies for temperature ranges, in quite good agreement with the two observed crystallization regimes.

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