CHAPTER 2. CRYSTALLISATION – THEORY AND EXPERIMENT

Some of the engineering thermoplastic polymers considered in this project have the potential of exhibiting crystalline characteristics, which may have a resultant effect upon the charge mobility. In addition, the introduction of the nanographite may add an additional level of complexity to the levels of crystallinity obtained. It is therefore important to have a thorough understanding of how these materials may behave upon processing.

2-1 Avrami Model[1-3]

Young and Lovell[3] have described polymer crystallisation as the process by which an ordered structure is produced from a disordered phase. Crystallisation is usually carried out either from a polymer solution or a melt. Crystallisation proceeds in two steps: nucleation and crystal growth. Nucleation can be either homogeneous or heterogeneous. During homogeneous nucleation, nuclei are formed randomly throughout the melt, whereas during heterogeneous nucleation the crystals are grown from inclusions such as impurities, fillers or fibres. The latter have the ability to absorb polymer chains onto their surface and can act as seeds for the crystal growth process.

Models used in the study of polymer crystallisation generally focus on predicting the development of crystallisation content as a function of time, and are usually based on the Avrami model, or a related form of the theory. As the rate of crystallisation is temperature dependent, it is clearly easier to study the behaviour under isothermal conditions. The Avrami model, which is effectively a geometric model, assumes that the overall crystallisation process can be considered as two distinct steps;

(I)   nucleation – the formation of the initial seed
(II)   crystal growth – the deposition of ordered chains on the initially formed seed.

The derivation of the model will now be described;

The rate of polymer crystallisation is dependent upon the nucleation rate and the resultant growth rate of spherulites. If we consider the rate of nucleation = N to be the number of nuclei produced per unit volume per unit time, then the number of nuclei formed per unit volume in a time interval dt is Ndt. If we consider a molten polymer mass of W_o, equivalent to a volume of W_o/ρ_l, where ρ_l is the density of the liquid polymer, then the number of nuclei formed in a specific time interval will be:

$$\frac{NW_0 dt}{\rho_l}$$
<div align="right">Equation 2-1</div>

Over time the spherulites will grow to have a radius, r and a volume of $\frac{4}{3}\pi r^3$. As $r = vt$, (where v is the rate of growth of the spherulite) it can also be written as $\frac{4}{3}\pi v^3 t^3$. For a solid (% crystalline) with a density, ρ_s, the mass of each spherulite can now be expressed as:

$$\frac{4}{3}\pi v^3 t^3 \rho_s$$
<div align="right">Equation 2-2</div>

Therefore, at time t, the total mass of spherulitic material will be

$$dW_s = \left(\frac{4}{3}\pi v^3 t^3 \rho_s\right)\left(NW_o \frac{dt}{\rho_1}\right)$$
<div align="right">Equation 2-3</div>

mass of spherulite   number of spherulites

Over a specific time, t the mass of all spherulites formed will be:

$$W_s = \int \frac{4\pi v^3 t^3 \rho_s NW_o}{3\rho_1} dt$$
<div align="right">Equation 2-4</div>

Integrating gives: $\dfrac{W_s}{W_o} = \dfrac{\pi N v^3 \rho_s t^4}{3\rho_1}$, which is the mass fraction of spherulites at time, t.

The mass of liquid remaining, $W_1 = W_o - W_s$:-

$$\frac{W_1}{W_o} = 1 - \frac{\pi N v^3 \rho_s t^4}{3\rho_1}$$
Equation 2-5

This highly simplified model, strictly valid only for the initial stages of crystallisation, shows that the mass fraction depends on t^4 and not t^3 as would be the case if the nucleation was instantaneous. One of the flaws with this analysis is that the model does not allow for the encroachment of the spherulites. To accommodate this impingement, the analysis can be further extended to give:

$$\frac{W_1}{W_0} = \exp(-zt^n) \text{ or } \left[1 - \frac{W_s}{W_0}\right] = \exp(-zt^n)$$
Equation 2-6

where z = constant. This is the *Avrami Equation*. The Avrami exponent, n, is dependent upon the nature of the crystal growth; generally Avrami exponents found experimentally for polymers range between 2 and 6 with most low molar mass polymers having an n value of 4. The value of n does not represent a unique set of nucleation and growth processes, though there is the possibility that a connection can be made between the n value, morphology, crystalline state and the crystallisation mechanism. It is important to note that n can be dependent upon the molar mass. Linear polyethylene of molar mass 4200 g mol^{-1} and 5800 g mol^{-1} have an n value of 4 – the crystallisation kinetics are therefore similar, or identical, for both. The growth behaviour can be represented by either rods or a rod-like assembly of the lamellar crystallites. For molar masses 7800 g mol^{-1} and 11500 g mol^{-1} crystallised at temperatures 129 and 130°C respectively, n is 4, but as the crystallisation temperature is lowered, $n = 3$. The crystallisation kinetics could be represented by spherulitic growth with instantaneous nucleation, or disc-like growth with time dependent nucleation. For higher molar masses of 3.8-8 x 10^6, $n = 2$; in this

case no well-defined superstructures are discerned and only randomly oriented lamellae that are not correlated with one another are observed. It should be noted that although the analysis assumes an integer value for the Avrami constant, in practice the value will often be non-integer, if there is a mixture of homogeneous and heterogeneous nucleation occurring.

Another flaw in the analysis is that the equation assumes crystallisation goes to 100 %, which is of course not the case for polymers. Generally, relative crystallinity values are quoted in order to overcome the problem. If a polymer is found to crystallise to an ultimate mass fraction, $w_c(\infty) < 1$ the Avrami analysis can be performed on this specific fraction. The Avrami equation becomes:-

$$(1 - x_r) = \exp\left(-\frac{1}{[1 - w_c(\infty)]} z t^n\right) = \exp(-kt^n) \qquad \text{Equation 2-7}$$

where x_r [= $w_c(t)/w_c(\infty)$] denotes the relative crystallinity for a time, t, k is the rate constant, $x_r = 0$ at start of crystallisation and $x_r = 1$ at end of the crystallisation. As stated above, $1 - x_r = \exp(-kt^n)$: Therefore,

$$\ln(1 - x_r) = -kt^n \qquad \text{Equation 2-8}$$

In order to test the Avrami plot experimentally, a plot of $\log(-\ln(1 - x_r))$ versus $\log t$ should give a straight line with gradient, n.

2-2 Non-Isothermal Crystallisation[4]

There has been a considerable amount of research devoted to the study of polymer crystallisation behaviour under isothermal conditions; however it is increasingly important to investigate the behaviour of semi-crystalline polymers under non-isothermal conditions, as the industrial processing of these materials is highly likely to involve a rate-dependent step.

2-2-1 Modified Avrami Model

A modified Avrami equation has also been frequently used to describe the non-isothermal primary crystallisation process. This has been done by applying the Avrami equation to analyse the data obtained from the non-isothermal crystallisation thermograms.

Most of the theories utilised in the area remain based on the Avrami equation, as detailed as Equation 2-6, with various modifications. Cooling from the melt is thought of as a succession of isothermal processes for a specific level of crystallinity at a specific time and temperature. A typical crystallisation isotherm can be seen in Figure 2-1. In region I the Avrami equation is obeyed. Although the Avrami continues along the dashed line in Region II, the actual crystallisation slows down and enters region III, the so called 'tail' region. Here crystallisation proceeds very slowly with time. In this region there is only a small percentage increase in the crystallinity level over many decades of time. The assumption of the Avrami model, namely that the crystallisation rate at time t is dependent only on the temperature and the relative crystallinity, and is independent of the crystallisation history, is valid as long as the non-isothermal crystallisation is restricted to region I in Figure 2-1. Graphs of % crystallinity versus temperature can then be plotted.
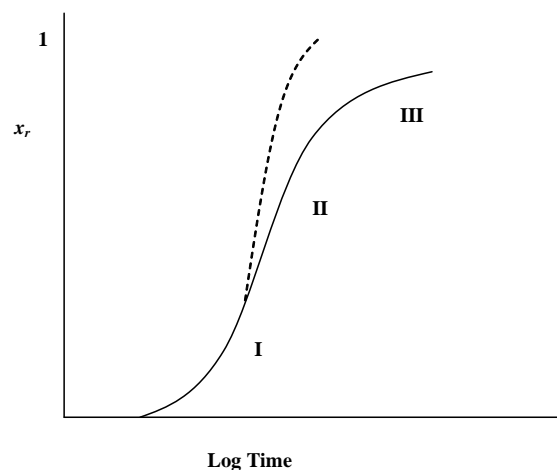

Figure 2-1 – Plot of degree of crystallinity against log time for a typical isotherm

Integration of the exothermic peaks during the non-isothermal scans gives the relative degree of crystallinity as a function of temperature. It is initially important to determine the temperature region over which crystallisation takes place and in doing so, convert the temperatures to time. Equation 2-9 was used for this purpose:-

$$\frac{\left|T_{onset} - T_{end}\right|}{a} \qquad \text{Equation 2-9}$$

where T_{onset} is the temperature at the start of crystallisation (°C) and T_{end} is the temperature at the end of crystallisation (°C) and a is the cooling rate (°C min^{-1}). On account of the non-isothermal conditions of the process, the value of crystallisation rate, Z_t, should be corrected as,

$$\log Z_c = \frac{\log Z_t}{a} \qquad \text{Equation 2-10}$$

where Z_c = crystallisation rate under isothermal conditions. A plot of log(-ln(1 - x_r)) versus log(t) can now be used in a similar way as for the isothermal model and will give the slope, n, the Avrami exponent, with the intercept being equal to log Z_t. It is noted that the n value obtained under non-isothermal conditions does not have the same physical meaning as that obtained under isothermal conditions. As the temperature changes continuously under non-isothermal conditions this has an effect upon the rate of both nuclei formation and spherulite growth.

2-2-2 Ozawa Model

One of the most commonly applied methods of analysis of non-isothermal crystallisation kinetics is the Ozawa model. This model assumed that the same process governs both isothermal crystallisation and non-isothermal crystallisation.

$$1 - x_r = \exp[-Z_t t^n] \qquad \text{Equation 2-11}$$

where, x_r is the relative crystallinity, Z_t is the crystallisation rate and n is the Avrami exponent.

When considering non-isothermal crystallisation there is a change of temperature with time, leading to the conclusion that the equation must account for time as a factor which affects the rate of crystallisation. Therefore, for a constant rate of temperature change $[(dT/dt) = \text{constant}]$ the Ozawa equation is as follows:

$$1 - x_r = \exp\left(\frac{-\kappa(T)}{|dT/dt|^n}\right)$$

Equation 2-12

where, $\kappa(T)$ is the cooling function of the non-isothermal crystallisation. $\kappa(T)$ is related to the overall crystallisation rate, and indicates how fast crystallisation occurs. Taking ln values followed by log gives the equation:

$$\log[-\ln(1 - x_r)] = \log[\kappa(T)] + n\log\left(\frac{1}{|dT/dt|}\right)$$

Equation 2-13

From Equation 2-13 it can be seen that if the Ozawa analysis is applicable, then a plot of $\log[-\ln(1 - x_r)]$ versus $\log\left|(dT/dt)^{-1}\right|$ should be linear, with a slope of n (corresponding to the Avrami constant) and an intercept of $\log \kappa(T)$. There are two factors that are ignored in the derivation of the Ozawa equation. Firstly, the slow secondary crystallisation is not considered; this could lead to a reduction in the obtained values of the Avrami parameters. Secondly, the change of the folding length of the polymer chain, which is a function of the crystallisation temperature, is also not considered. If this length decreases with a decrease in crystallisation temperature, the effect should not be negated.

The Ozawa model has been successfully applied to poly(ethylene terephthalate) at low cooling rates,[5] and poly(phenylene sulfide),[6] but in the case of PEEK[7] and PEKK[8] non-linearity has been reported. This non-linearity has been attributed to secondary

crystallisation; the changing slopes show that n is not constant with temperature during the primary crystallisation process.

2-2-3 Combined Ozawa/Avrami Model

Liu *et al*.[8] developed a method to allow the Ozawa and Avrami models to be combined into a single formula, seen in Equation 2-14 and Equation 2-15.

$$\log Z_t + n\log \text{t} = \log K(T) - m\log(a) \qquad \text{Equation 2-14}$$
$$\log a = \log F(T) - b\log(t) \qquad \text{Equation 2-15}$$

where $F(T)$ is equal to $[K(T)/Z_t]^{1/m}$ and b is equal to n/m, the ratio of the Avrami and Ozawa exponents. The physical meaning of the rate parameter $F(T)$ refers to the necessary value of cooling rate to reach a defined degree of crystallinity at unit crystallisation time. A plot of $\log(a)$ against $\log(t)$ should give a linear relationship, with intercept of $\log F(T)$ and a slope of $-b$.

2-3 Experimental

2-3-1 Materials

The materials utilised in this chapter are PEEK and nanographite. The synthesis of PEEK is discussed in Section 2-3-2. Graphite 3775 was the nanographite material used in this study (supplied by Asbury Graphite Mills, USA). It is an intercalated natural flake graphite which has been exfoliated, compressed, and then milled to an average particle size of 5-7 micrometres. The surface area has been increased over that of an equivalent grade of untreated natural flake graphite of the same particle distribution.

2-3-2 Synthesis of PEEK (synthesis was carried out by Cytec)

The synthesis of PEEK was deemed to be proprietary and therefore the details are not available for disclosure in the thesis. In general terms, the synthetic procedure involved heating 4,4'-diflorobenzophenone and hydroquinone in the presence of potassium carbonate and a suitable solvent, in order to achieve solubilisation of the starting materials. The reaction mixture was then suitably heated to achieve polymerisation, as indicated in Figure 2-2. The polymer was then dried under vacuum at 100°C for 24 hours.
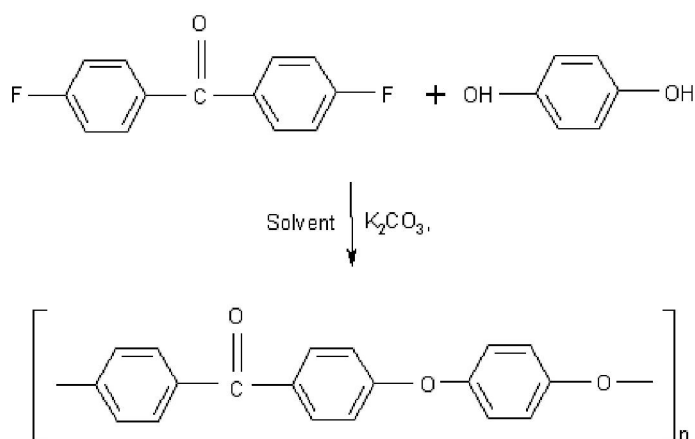

Figure 2-2 – Synthesis of PEEK

2-3-3 Additional Note

It is noted at this point that the presence of impurities within the PEEK samples have the potential to act as nucleating agents; potentially through the use of solvent in the synthesis. In a paper by Kumar and Anderson[9] it was stated that even purification using sulfuric acid leads to the presence of impurities in the starting materials used. They found them to be in the form of other species of the poly(ether ether ketone) family.

2-3-4 DSC

The crystallisation of the polymers was studied using differential scanning calorimetry. Measurements were performed using a TA Q1000 DSC which is capable of being used in a modulated mode. The instrument has been calibrated to be within 0.5°C of the actual required temperature. Two types of measurement were carried out:-

2-3-4-1 Isothermal Crystallisation

The crystallisation behaviour of PEEK, PEEK + 3 % nanographite and PEEK + 10 % nanographite was studied under isothermal conditions. Sample sizes in the range of 3-5 mg were used, to minimize the effects of low thermal conductivity. Samples were heated to 400°C at 40°C min^{-1} before cooling at 80°C min^{-1} to an isothermal crystallisation temperature of between 305 and 330°C. The temperature was held isothermally for 60 minutes before equilibrating at 50°C and then the samples were reheated at 10°C min^{-1} to 400°C.

2-3-4-2 Non-Isothermal Crystallisation

The crystallisation behaviour of PEEK, PEEK + 3 % nanographite and PEEK + 10 % nanographite was also studied under non-isothermal conditions. Sample sizes in the range of 3-5 mg were used, again, to minimize the effects of low thermal conductivity of

the polymer. Samples were heated at 10°C min^{-1} to 400°C before cooling to 50°C at a defined rate, (from 1°C min^{-1} to 80°C min^{-1}) and then reheated at 10°C min^{-1} to 400°C.

2-4 References

1. L. Mandelkern, *Crystallisation of Polymers: Second Edition, Volume 2*. 2004, McGraw Hill

2. J.J. Liggat, *Final year Polymer Crystallisation Lecture note*, 2006.

3. R.J. Young, P.A. Lovell, *Introduction to Polymers*. 1991, Chapman and Hall

4. D.L. Bower, *An Introduction to Polymer Physics*. 2002, Cambridge University Press

5. P. Sajkiewicz, L. Carpaneto, A. Wasiak, *Application of the Ozawa model to non-isothermal crystallization of poly(ethylene terephthalate)*. Polymer, 2001. **42**(12): p. 5365-5370.

6. L.C. López, G.L. Wilkes, *Crystallization kinetics of poly(p-phenylene sulphide): effect of molecular weight*. Polymer, 1988. **29**(1): p. 106-113.

7. P. Cebe, S.D. Hong, *Crystallisation Behaviour of Poly(ether-ether-ketone)*. Polymer, 1986. **27**: p. 1183-1192.

8. T. Liu, Z. Mo, S. Wang, H. Zhang, *Nonisothermal melt and cold crystallization kinetics of poly(aryl ether ether ketone ketone)*. Polymer Engineering & Science, 1997. **37**(3): p. 568-575.

9. S. Kumar, D.P. Anderson, *Crystallisation and morphology of poly(aryl-ether-ether-ketone)*. Polymer, 1986. **27**(3): p. 329-336.