CHAPTER 3. CRYSTALLISATION – RESULTS AND DISCUSSION

3-1 Introduction

The main objective of this thesis is to explore the possibility of enhancing the electrical conductivity of a thermoplastic matrix by the addition of nanoscale conducting particles. In Chapter 2 it was shown that impurities can act as nucleating agents for crystallisation. In practice, the incorporation of the nanomaterials will involve melting of the polymer, and the subsequent cooling process will influence the degree of crystallinity of the thermoplastic component of the composite produced. Crystallinity has the possibility of inhibiting charge carrier migration, and therefore is an important factor in controlling the conductivity of the composite. It is therefore important to study crystallisation behaviour of these systems when nanoparticles are present. The crystallinity may be expected to influence the percolation path for conducting entities, and hence the ability to achieve acceptable levels of electrical conductivity. It is therefore important to understand the effect that the incorporation of the nanoparticles has upon the resultant crystallinity under isothermal conditions. In practice, however, the behaviour of semi-crystalline polymers under non-isothermal conditions more closely replicates industrial processes such as dynamic cooling, which would occur during composite production and more specifically fibre formation. Therefore this study will look at the effects of the nanographite under both conditions.

3-2 Materials

The material studied in this chapter was PEEK [poly(ether ether ketone)] which is doped with nanographite. The synthesis of the PEEK is discussed in Section 2-3-2, and the discussion relating to the synthesis of nanographite is outlined in Section 2-3-1.

3-3 An Initial Note on Errors

As discussed in the theory and experimental section, Chapter 2, the DSC has been calibrated to ensure that reported temperatures are to within ±0.5°C of the reported temperature.

In addition, another potential source of error which must be considered is that of the reported crystallisation times of the DSC studies. By considering the raw data obtained it could be ascertained that the error associated with time, in order to be within half a degree of the isothermal temperature under study, is 0.5 minute. There will also be a quantifiable error associated with the n and k values reported. From careful consideration of the accuracy of determination of the linear portion of the Avrami plot it is concluded that a 5 % error should be attributed to this. With regards to the enthalpies quoted in this chapter it is concluded that, after careful consideration of the determination of the area under the graphs responsible, a 5 % error should be attributed. Regarding the combined Ozawa/Avrami study there will be a quantifiable error associated with the linearity, or non-linearity of the plots. From careful consideration of this error it is decided to attribute a 10 % error to the reported values of $F(T)$ and b.

3-4 Results

3-4-1 Isothermal Studies

Crystallisation Isotherms – The crystallisation behaviour of PEEK, PEEK + 3 % nanographite and PEEK + 10 % nanographite was studied under isothermal conditions, according to the method discussed in Section 2-3-4-1. Overlaid DSC thermograms showing typical crystallisation behaviour of the three systems under study, at 325°C, can be seen in Figure 3-1. Interestingly, it can be seen that there are two distributions of crystallisation regimes present. The PEEK scan shows a diffuse crystallisation exotherm which takes a considerable time to tail-off. The PEEK + 10 % nanographite scan shows the exotherm to occur over a short time period with no tail-off. It should also be noted that crystallisation starts very early, after approximately three minutes. The PEEK + 3 % nanographite scan has elements of both behaviours present; the exotherm starts at a similar time for the 10 % blend, but occurs over a longer period before tailing off in a similar manner to that observed in pure PEEK. The times to reach the peak maximum, t_p, are detailed in Table 3-1 where the time presented, in each case, is an average of three measurements. From Table 3-1 it can be seen that in each case, the time to reach maximum crystallinity becomes less as more nanographite is introduced into the system. This effect was reported by Kalaitzidou *et al.*[1] When they introduced nanographite into a polypropylene matrix. In their study, they commented on the fact that the number of nucleation sites increases with nanographite concentration. Upon consideration of Figure 3-1 it can be seen that PEEK takes 25.6 minutes, PEEK + 3 % nanographite takes 8.8 minutes and PEEK + 10 % nanographite takes 6.6 minutes to reach the maximum rate of heat release, at 323°C. It is therefore clear that even a small level of nanographite is having a large nucleating effect upon the polymer. In addition, the area under each curve was calculated and was found to be 21.2 J g^{-1} for the neat polymer, 51.9 J g^{-1} for the polymer + 3 % nanographite and 53.6 J g^{-1} for the polymer + 10 % nanographite. The enthalpy of crystallisation is significantly changing and therefore indicates that the isothermal crystallisation behaviour is also undergoing significant changes with the inclusion of the nanographite.

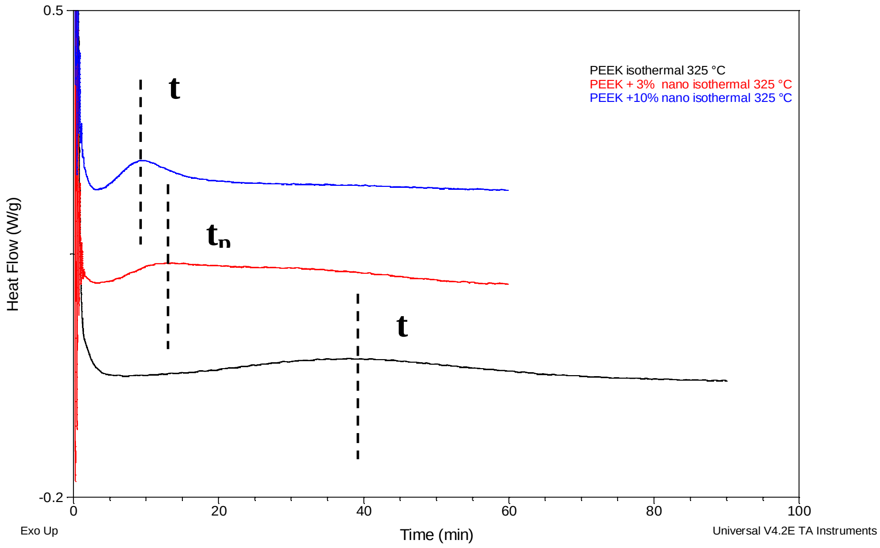

Figure 3-1 – DSC isothermal scans of PEEK, PEEK + 3 % nanographite and PEEK + 10 % nanographite at 325°C

In order to look at the nucleating effect that the nanographite is having upon the PEEK, a more detailed graph was plotted showing the time to reach maximum rate of crystallisation, $t_{p,}$ versus temperature for each polymer system under investigation. The graph is shown in Figure 3-2. Again, the nucleating effect of the nanographite can be clearly seen. It can also be seen that the 10 % polymer system shows only a slight decrease in the time to reach t_p when compared with the 3 % system. The difference in the times of these two systems becomes greater at higher temperatures. This again demonstrates the fact that relatively low levels of nanographite are having a large nucleating effect.

Table 3-1 – Crystallisation times for each polymer system

Polymer system	**Temperature (°C)**	**Time to reach peak maximum, t_p (min)**
PEEK	305±0.5	2.8±0.5
PEEK	310±0.5	4.8±0.5
PEEK	315±0.5	8.3±0.5
PEEK + 3 % nanographite	315±0.5	2.7±0.5
PEEK +10 % nanographite	315±0.5	2.1±0.5
PEEK	320±0.5	16.8±0.5
PEEK + 3 % nanographite	320±0.5	5.4±0.5
PEEK +10 % nanographite	320±0.5	4.1±0.5
PEEK	323±0.5	25.6±0.5
PEEK + 3 % nanographite	323±0.5	8.9±0.5
PEEK + 10 % nanographite	323±0.5	6.6±0.5
PEEK	325±0.5	37.5±0.5
PEEK + 3 % nanographite	325±0.5	13.4±0.5
PEEK + 10 % nanographite	325±0.5	9.5±0.5
PEEK + 3 % nanographite	330±0.5	36.0±0.5
PEEK + 10 % nanographite	330±0.5	26.4±0.5

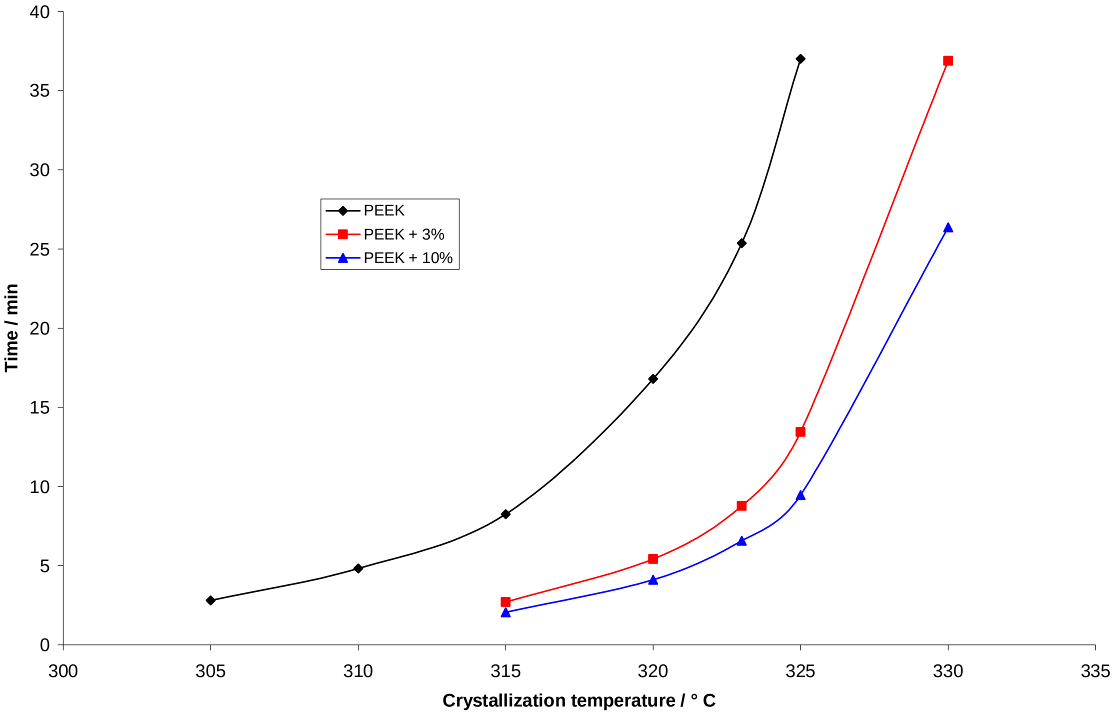

Figure 3-2 – Time to maximum of crystallisation exotherm vs. crystallisation temperature for each polymer system

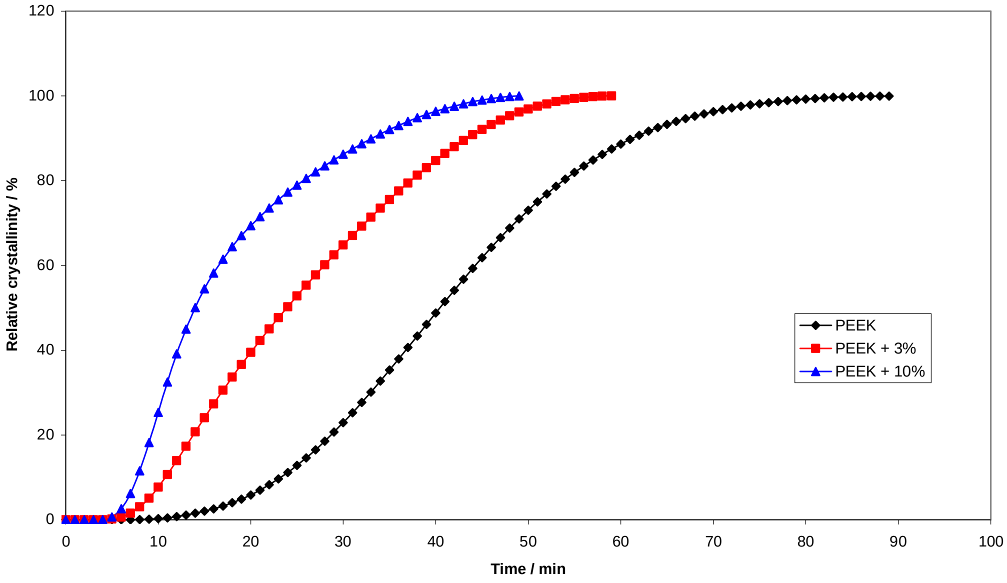

Figure 3-3– Development of crystallinity with time for isothermal crystallisation at 325°C for PEEK, PEEK + 3 % nanographite and PEEK + 10 % nanographite

The relative amount of crystallinity that developed over time, normalized to 100 % has been plotted for the three systems at 325°C, and can be seen in Figure 3-3. Development of the relative crystallinity can be analysed using the Avrami equation, discussed in Section 2-1. This development is detailed in the following section.

3-4-1-1 Avrami Analysis

Development of the relative crystallinity was analysed using the Avrami equation, which was discussed in Section 2-1. Plots of $\log(-\ln(1 - x_r))$ versus $\log(t)$ for temperatures 320, 323, 325, and 330°C were plotted and are shown in Figure 3-4, Figure 3-5, Figure 3-6 and Figure 3-7. It can be seen from the graphs that below 323°C the nanographite samples were found to crystallize too quickly for a reliable Avrami analysis to be made, and above 325°C PEEK crystallized too slowly; therefore only scans carried out at 323°C and 325°C are displayed for all three materials. It can be seen that each curve has a linear portion followed by a roll-off at longer times. It must be noted that there is a tendency to deviate from this linearity with the introduction of increasing quantities of nanographite.

Fitting the initial linear portion of $\log(-\ln(1-x_r))$ versus $\log(t)$ for times before the roll off, allows the determination of n and k from Equation 2-7. Table 3-2 presents a summary of the parameters found from measurements of crystallisation carried out under isothermal conditions. It is noticed that in the case of the PEEK samples the range of the initial linear portion of the curve occurs over a much larger range, typically at least 50 %. With the introduction of the nanographite the initial linear portion is confined to only the first 19-20 % of the graph. It is therefore apparent that the introduction of the graphite is having a significant effect upon the Avrami analysis.

It can be seen that the Avrami exponent, n – considering each temperature separately – is moving to higher values with the introduction of more nanomaterial into the system, this suggests that the morphology of the growing spherulite is becoming more complicated. For example, considering the results at 323°C, the value of n moves from an average of 3.4 for the neat PEEK, to 4.2 for the PEEK + 3 % nanographite, and to 5.8 in the case of PEEK + 10 % nanographite. Although the value of *n* does not represent a unique set of nucleation and growth processes, the significant differences reported here indicate that the kinetics of the crystallisation process are changing significantly with the introduction of the nanographite. If the growth process were to stay the same then the index *n* would be expected to have remained constant; the fact that it changes is indicative of a change in the growth mechanism. It would appear that the growth of the spherulite is moving from a heterogeneous nucleation with three dimensional growth, to a sheaf-like growth mechanism.

Considering the *n* values from the PEEK graphs, it can be seen that there is a significantly small change occurring in the values at the different temperatures studied, going from an average of 3.4 at 320°C to 3.7 at 325°C. This is indicative of a simultaneous nucleation process occurring in each case, with the spherulitic growth of crystals, and is consistent with results reported by Cebe and Hong.**[2]** Indeed the Avrami constant reported by them at 315°C is very similar to that reported in this study at 320°C – 3.3 c,f. 3.4. The Avrami constant reported in both studies for PEEK is consistent with heterogeneous nucleation and three dimensional spherulitic growth. For the PEEK + 3 % nanographite there is, again, a relatively small change occurring within the temperature range under investigation, going from 4.1 at 320°C to 4.0 at 325°C, again indicating a three dimensional heterogeneous nucleation process. When considering the PEEK + 10 % nanographite results it can be seen that there is a shift from an Avrami exponent of 5.8 to a value of 4.0 at 330°C; although it must be stated that there is no homeogenous nucleation possible at the higher temperature as PEEK crystallises too slowly. It is therefore concluded that PEEK + 10 % nanographite moves from a heterogeneously nucleated sheaf-like morphology at the lower temperatures of 323 and 325°C to a spherical morphology when no homeogenous nucleation is possible at 330°C.

It is noted that the sample examined in the DSC experiment has typically a volume of 2.9 x 10^{-3} cm^3 (a density of 1.37 g cm^{-3} and a mass of 4 mg is assumed for PEEK). This volume translates to a diameter of ~0.13 cm. The nanographite has a length in the region of tens of microns (or ~1 x 10^{-3} cm); therefore if the nanographite platelets were to sit side by side ~ 130 may be expected. Having said this, it is still nonetheless very difficult - within these small volumes - to ensure that the sample examined is homogeneous. It is probable that there will be local differences within the dispersions which may be reflected in the variations in the data. The data presented are an average of three measurements and significant differences were observed between samples in the case of some of the higher graphite loadings. The values presented in the thesis are an average of those obtained.

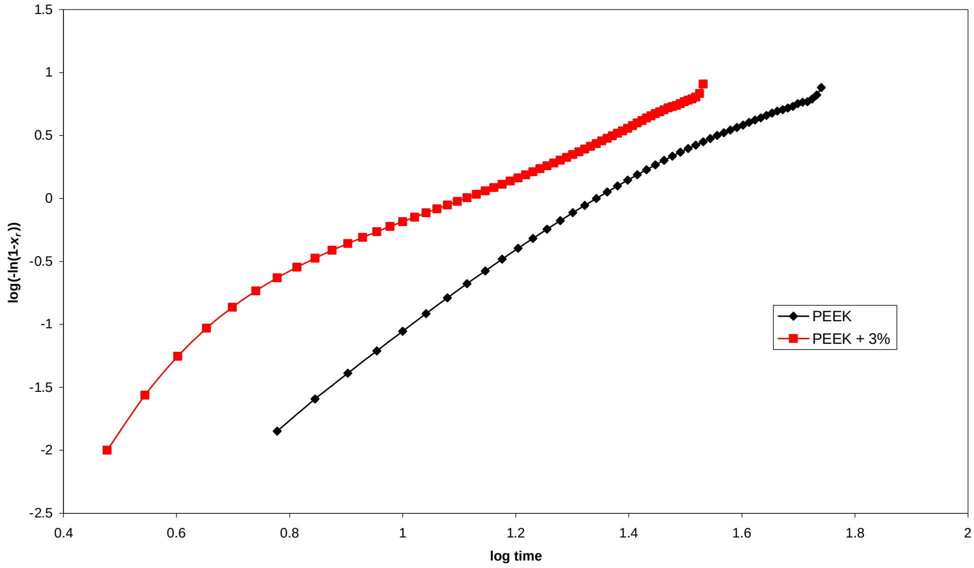

Figure 3-4 – Avrami plots, isothermally crystallized at 320°C

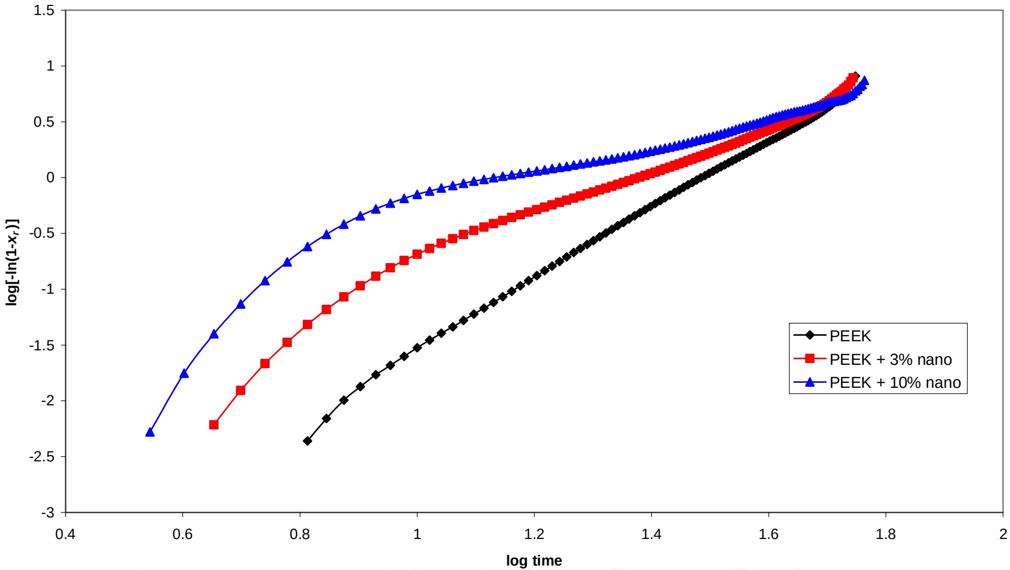

Figure 3-5 – Avrami plots, isothermally crystallized at 323°C

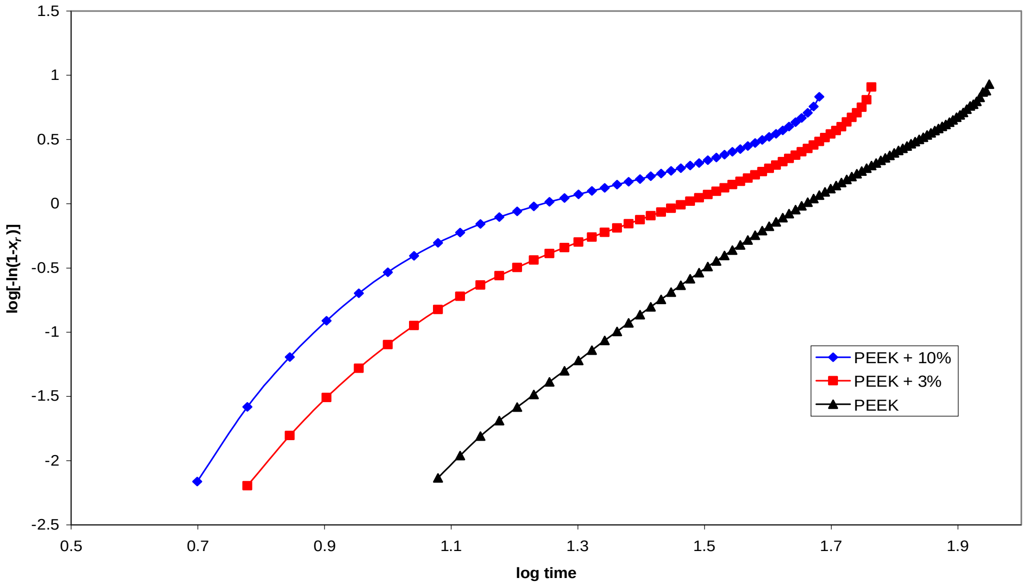

Figure 3-6– Avrami plots, isothermally crystallized at 325°C

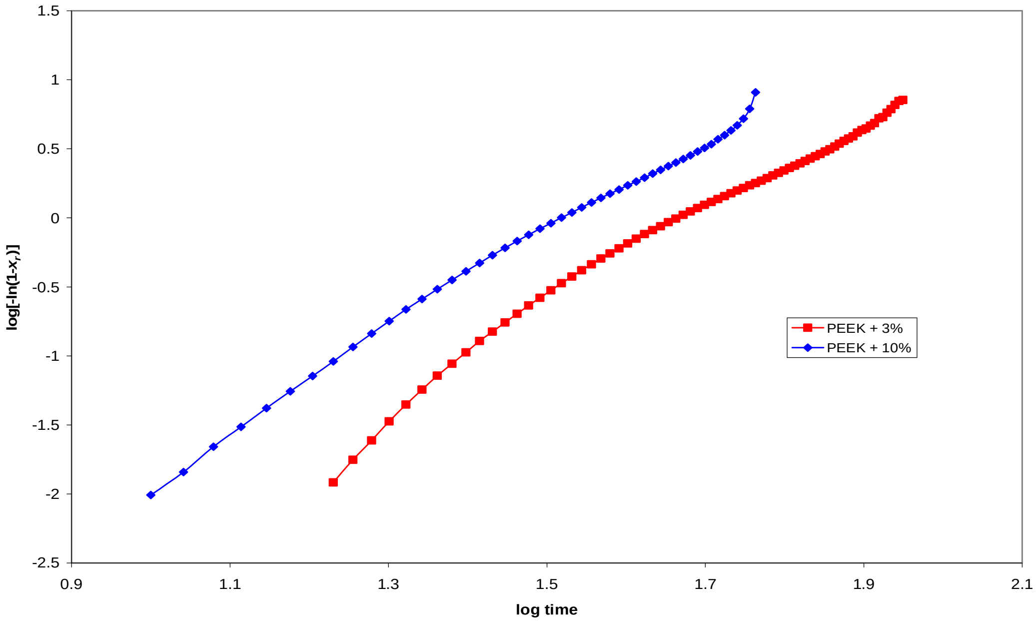

Figure 3-7 – Avrami plots, isothermally crystallized at 330°C

Table 3-2 – Parameters *n* and *k* from the Avrami analysis of isothermal crystallisation

	Avrami Value (*n*)	Intercept	R^2	Rate Constant (*k*)	Range
320°C					
PEEK					
1	3.4	-10.441	0.996	4.008 x 10^{-3}	49
2	3.1	-9.131	0.991	9.041 x 10^{-3}	49
3	3.6	-10.696	0.998	2.002 x 10^{-3}	51
PEEK + 3% nanographite					
1	4.1	-10.748	0.984	1.613 x 10^{-2}	19
2	4.0	-10.874	0.983	1.715 x 10^{-2}	20
3	4.3	-11.204	0.988	1.207 x 10^{-2}	19
323°C					
PEEK					
1	3.7	-12.581	0.999	1.001 x 10^{-3}	50
2	3.2	-11.027	0.999	1.001 x 10^{-3}	52
3	3.2	-10.960	0.999	1.001 x 10^{-3}	52
PEEK + 3% nanographite					
1	4.0	-10.654	0.90	1.054 x 10^{-1}	19
2	4.3	-11.303	0.98	2.020 x 10^{-2}	19
3	4.3	-11.193	0.98	2.020 x 10^{-2}	19
PEEK + 10% nanographite					
1	6.4	-12.857	0.982	1.816 x 10^{-2}	19
2	5.9	-12.217	0.987	1.309 x 10^{-2}	20
3	5.2	-10.780	0.993	7.025 x 10^{-3}	19
325°C					
PEEK					
1	3.8	-14.493	0.997	3.005 x 10^{-3}	51
2	3.4	-12.624	0.998	2.002 x 10^{-3}	50
3	3.9	-14.812	0.997	3.005 x 10^{-3}	52
PEEK + 3% nanographite					
1	3.9	-11.684	0.980	2.020 x 10^{-2}	20
2	4.0	-11.772	0.992	8.032 x 10^{-3}	20
3	4.0	-11.734	0.989	1.106 x 10^{-2}	21
PEEK + 10% nanographite					
1	5.3	-13.363	0.988	1.207 x 10^{-2}	20
2	5.2	-12.476	0.989	1.106 x 10^{-2}	21
330°C					
PEEK + 3% nanographite					
1	4.5	-16.849	0.989	1.106 x 10^{-2}	51
2	5.2	-18.932	0.994	6.018 x 10^{-3}	21
PEEK + 10% nanographite					
1	3.9	-13.514	0.999	1.001 x 10^{-3}	51
2	4.2	-14.400	0.997	3.005 x 10^{-3}	49

3-4-1-2 Melting Behaviour Following Isothermal Crystallisation

The first melting endotherms of PEEK were reported by Blundell and Osborn.[3] Endothermic peaks shown in their study are not identical to those reported in this study;

see DSC thermograms of the re-heating cycle following isothermal crystallisation for PEEK, PEEK + 3 % nanographite and PEEK + 10 % nanographite in Figure 3-8, Figure 3-9 and Figure 3-10, respectively. This is unsurprising as small variations in molecular microstructure, molecular mass distribution and the presence of additives may significantly affect the phase transition kinetics. Therefore, for each polymer, even within a single batch, it is important to perform precise determinations of crystallisation kinetics.

It can be seen from the figures that the traces are characterized by two, distinct, melting processes – the temperatures of both peaks for all isothermal scans are detailed in Table 3-3. This double melting process has been reported to develop from two distinct crystal growth mechanisms.[4] These mechanisms correspond to spherulitic and epitaxial (or secondary) crystal growth and melting. Spherulites form more rapidly than the epitaxial crystals, and therefore, represent the more dominant growth mechanism. Epitaxial crystals are small crystal-aggregate-like structures, which form from the remaining uncrystallized fraction. The amount of these crystallites depends on the remaining uncrystallized material. The mobility of the surrounding amorphous material is reduced during spherulitic crystal growth thus limiting the growth of epitaxial crystals. It is noted at this point that during the crystallisation process there will be some fractionation of the material and hence the precise distribution between spherulitic and epitaxial growth can also reflect differences in the molar mass distribution of the polymer sample. These polymers are produced by a condensation reaction and have a broad molar mass distribution.

It can be seen that there is a smaller, low-temperature peak followed by a larger peak that occurs at a higher temperature. The lower peak has been attributed to the melting of crystalline regions formed during the previous isothermal crystallisation. It is characteristic of the majority of the crystals present in the sample at room temperature, prior to the start of the re-heat run. As the scan progresses it has been proposed that the polymer is going through continually competing re-crystallisation and melting processes. It can be seen from the table that the temperatures of the lower melting process are not significantly affected by the inclusion of the nanographite. Consider the material isothermally crystallized at 315°C; for neat PEEK the temperature of the peak is 322.1°C. In the case of both 3 % nanographite and 10 % nanographite the temperature found was 322.2°C.

The upper melting process is also hardly affected by the addition of the nanographite. Considering, again, the 315°C isothermally crystallized systems, the temperature of this peak is seen to occur at 345.8°C for the neat PEEK; it occurs at 346.2°C when considering the PEEK + 3 % nanographite, and 345.6°C when considering PEEK + 10 % nanographite.

The enthalpy of melting was determined for all the re-heat graphs, with resultant values displayed in Table 3-3. It can be seen that the enthalpy values increase as the isothermal temperature is reduced. Considering the neat PEEK curves it is seen that at 325°C the enthalpy value is 60.4 J g^{-1}. When the isothermal temperature is reduced to 305°C the resultant enthalpy value shifts to 65.9 J g^{-1}. In addition it can be seen that for the same isothermal temperature, the enthalpy values decrease significantly with the addition of nanographite. Considering the values at 315°C it is seen that for the neat PEEK the enthalpy is 64.7 J g^{-1}, this shifts to 62.3 J g^{-1} in the case of the 3 % nanographite, and 57.1 J g $^{-1}$ in the case of the 10 % nanographite. These scale with the amount of actual polymer present.

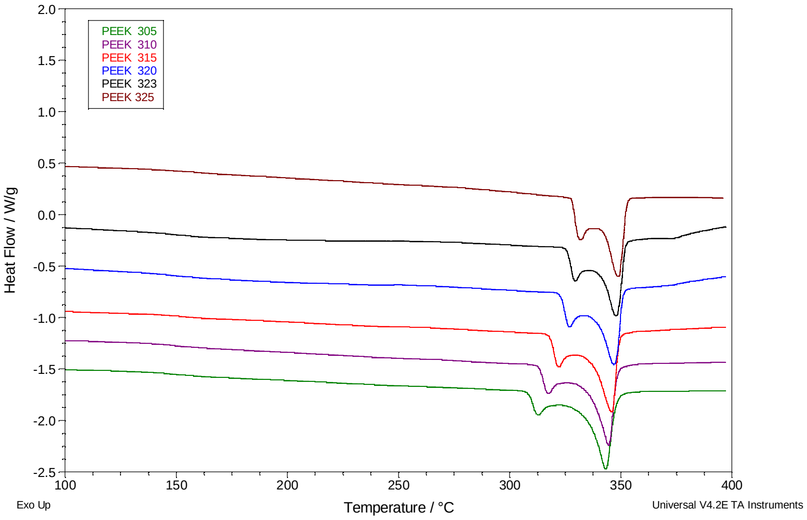

Figure 3-8 - Overlaid DSC reheat curves for PEEK

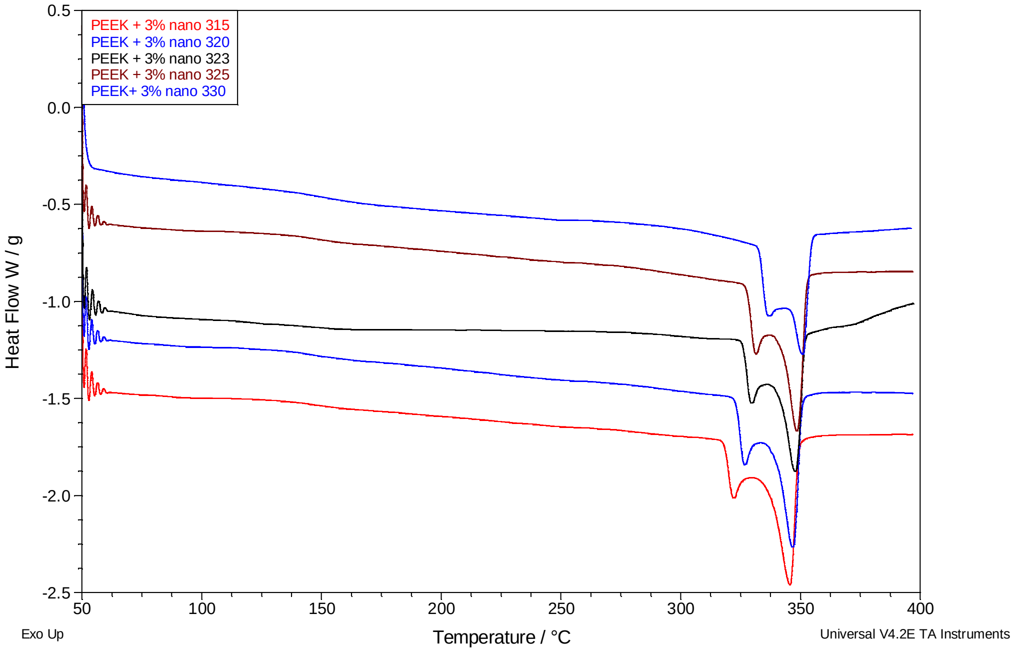

Figure 3-9 - Overlaid DSC reheat curves for PEEK + 3 % nanographite

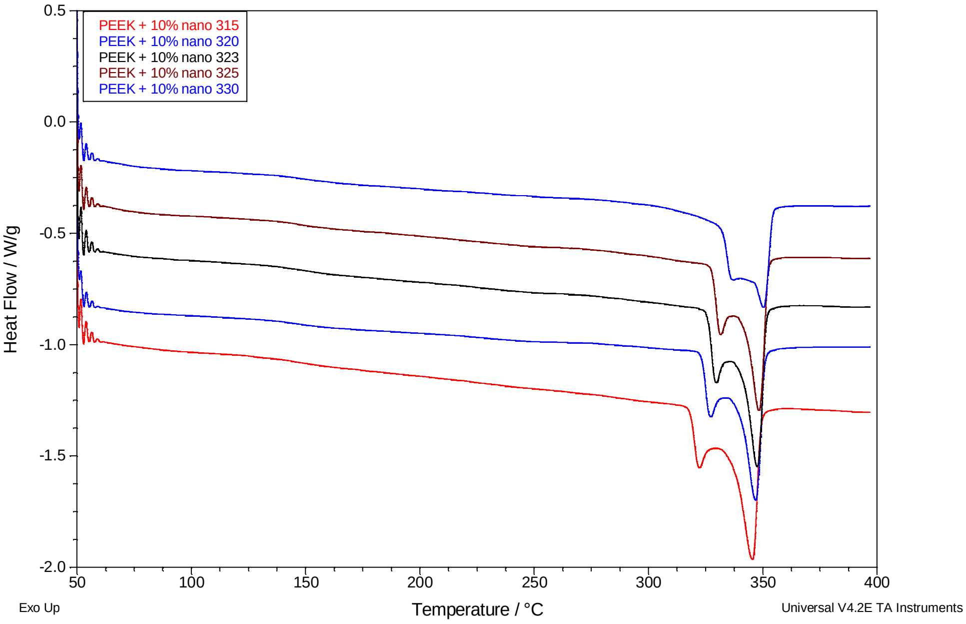

Figure 3-10 - Overlaid DSC reheat curves for PEEK + 10 % nanographite

Table 3-3 – DSC peak positions

Sample	**Isothermal Temperature (°C)**	**T_{lower} (°C)**	**T_{upper} (°C)**	**ΔH_{melt} ($J\ g^{-1}$)**
PEEK	305±0.5	312.7±0.5	343.1±0.5	65.9±3.3
	310±0.5	317.2±0.5	344.0±0.5	65.8±3.3
	315±0.5	322.1±0.5	345.8±0.5	64.7±3.2
	320±0.5	326.1±0.5	346.7±0.5	60.5±3.0
	323±0.5	329.3±0.5	347.6±0.5	60.5±3.0
	325±0.5	331.5±0.5	348.9±0.5	60.4±3.0
PEEK + 3 % nanographite	315±0.5	322.2±0.5	346.2±0.5	62.3±3.1
	320±0.5	326.3±0.5	346.7±0.5	62.1±3.1
	323±0.5	329.5±0.5	347.7±0.5	61.3±3.1
	325±0.5	331.5±0.5	348.2±0.5	61.0±3.1
	330±0.5	336.2±0.5	350.3±0.5	53.5±2.7
PEEK + 10 % nanographite	315±0.5	322.2±0.5	345.6±0.5	57.1±2.9
	320±0.5	327.4±0.5	346.7±0.5	53.2±2.7
	323±0.5	329.5±0.5	347.7±0.5	53.6±2.7
	325±0.5	331.0±0.5	348.2±0.5	50.2±2.5
	330±0.5	336.2±0.5	349.8±0.5	44.2±2.2

3-4-2 Non-Isothermal Results

3-4-2-1 Crystallisation Behaviour

As outlined in Section 2-2, the crystallisation behaviour of PEEK, PEEK + 3 % nanographite and PEEK + 10 % nanographite was studied under non-isothermal conditions. The overlaid DSC thermograms of the cool cycle of the heat-cool-reheat sequences for the DSC runs of the PEEK, PEEK + 3 % nanographite and PEEK + 10 % nanographite can be seen in Figure 3-11, Figure 3-12 and Figure 3-13 for all of the cooling rates. The PEEK curves can be seen in Figure 3-11, where in all cases a single, symmetrical, exothermic peak is detected, regardless of cooling rate. When one considers a sample of pure polymer, crystallisation would be expected to be initiated by homogeneous nucleation with the formation of large spherulites, especially under slow nucleation conditions. The peak height and area appear to increase with increasing cooling rate. This is due to the heat flow being defined as the exothermic heat per unit time. For all polymer systems studied it is seen that the value of the crystallisation exotherm peak shifts to lower temperatures as the cooling rate increases, for example, going from 314°C to 264°C when one considers PEEK at a cooling rate of 1°C min^{-1} and 80°C min^{-1}, respectively – the peak also becomes broader.[5]

Values of the crystallisation temperature on cooling (T_{cc}) and enthalpy of crystallisation (ΔH_{cryst}) are detailed in Table 3-4. It can be seen from the table that the crystallisation temperature of the polymer is increased significantly by the addition of the nanographite. When one considers the highest cooling rate of 80°C min^{-1} it is seen that the T_{cc} values are shifted considerably, going from 264°C in the case of PEEK, to 290°C in the case of both PEEK + 3 % nanographite and PEEK + 10 % nanographite. These results clearly show that the nanographite is acting as a nucleating agent.

When one considers the DSC curves of the PEEK + 3 % nanographite and PEEK + 10 % nanographite depicted in Figure 3-12 and Figure 3-13, it is seen that in this case the curves are asymmetric; this could be due to phase transformations[5] or the most dominant of different crystallisation mechanisms occurring when the nanographite is present. It would certainly appear that the crystallisation kinetics are becoming more complex with the addition. Non-conventional DSC curves in other multi-phase-separated systems have been reported in the literature,[6] where multiple exothermic peaks were found to arise from phase-separated components, with the crystallisable component confined to small droplets, and the available heterogeneities being segregated into a small portion of the droplets. In these systems crystallisation is delayed in the remaining heterogeneity-free domains, as the crystal growth starts from homogeneous nuclei. It is noted at this point that the nanomaterial is tumble blended with the PEEK and it is therefore unsurprising that there are areas of the PEEK which are not in intimate contact with the nanographite, hence leading to the more complex crystallisation behaviour. There appears to be less asymmetry present in the 10 % nanographite curves, most likely due to the fact that more nanomaterial is present for the polymer to be in close contact with. A paper from Li *et al.*[7] stated that there are two kinds of growth morphology associated with the bulk crystallisation of the PEEK; transcrystallinity near a heterogeneous surface and self-seeded cart wheel spherulites. Both are spherulitic in nature and it is proposed that the effect of transcrystallinity is responsible for the different shapes of the graphs

When considering the ΔH_{cryst} values it can be seen that the enthalpy values decrease with increased cooling rates, as would be expected. As the crystals form at the highest cooling rates there is no time to form perfect lamellae, so the enthalpy change upon crystallisation is found to decrease as the cooling rate increases. Looking at the 1°C min^{-1} results, it can be seen that the values obtained are 68, 66 and 59 J g^{-1} for the neat polymer, the polymer + 3 % nanographite and polymer + 10 % nanographite, respectively. It is proposed that this reduction scales simply with the reduced polymer content in the nanographite blends, which would indicate that the crystallinity of the polymer (ca 50 %) is unchanged by the presence of the nanomaterial. In order to allow for the fact that not all samples have the same level of crystallizable polymer present, ΔH values of nanographite containing samples were adjusted accordingly. In order to determine the net crystallinity values, all ΔH values were subsequently divided by the accepted value of 130 J g^{-1} – which corresponds to the heat of fusion of perfectly crystalline PEEK.[3] Corrected values can be seen in the final column of Table 3-4.

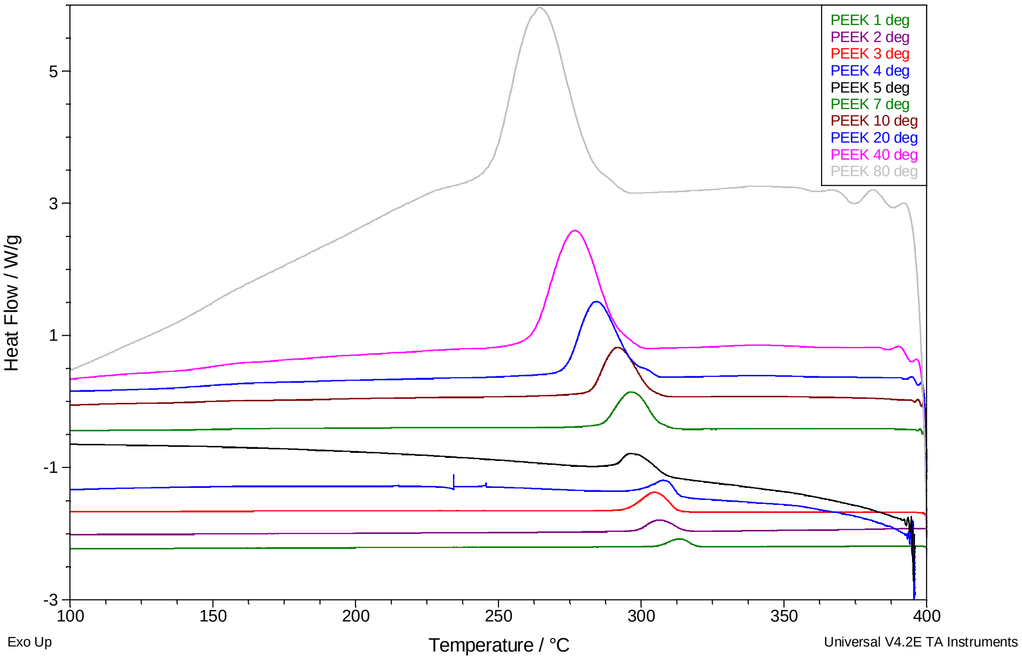

Figure 3-11 – Overlaid DSC cooling curves of PEEK

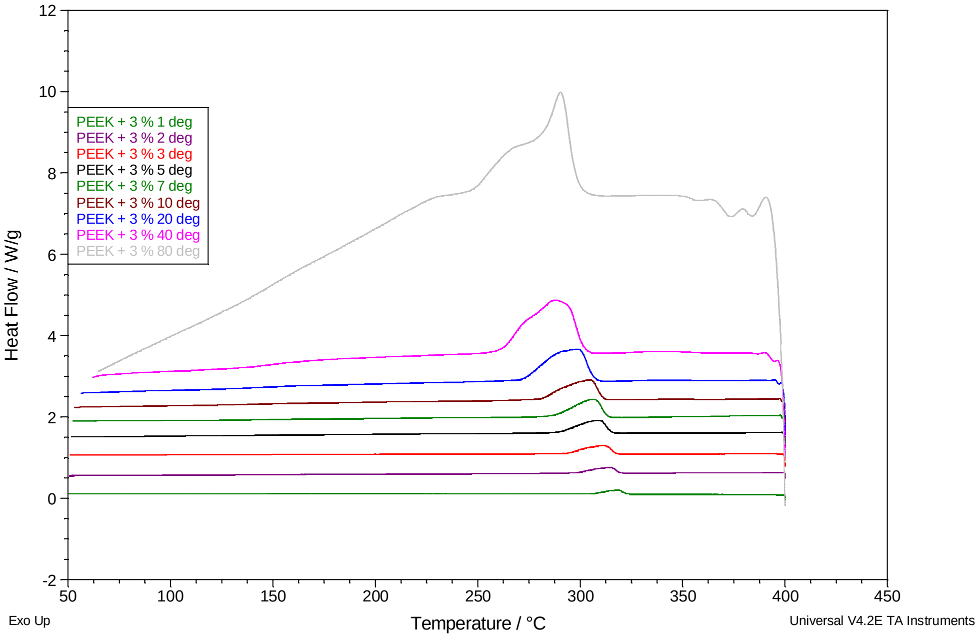

Figure 3-12 Overlaid DSC cooling curves of PEEK + 3 % nanographite

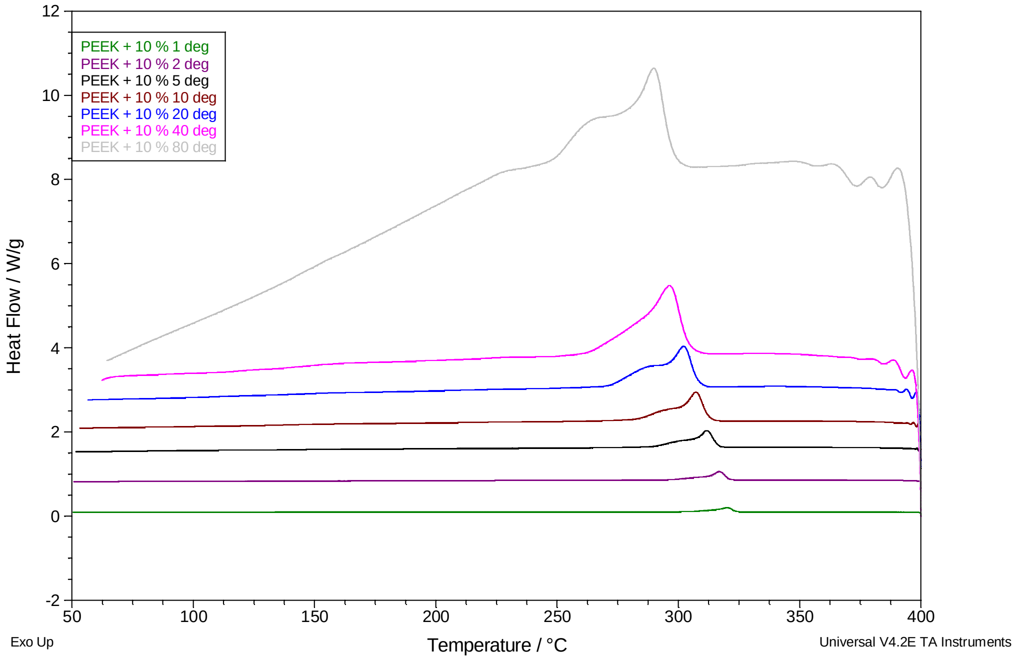

Figure 3-13– Overlaid DSC cooling curves of PEEK + 10 % nanographite

3-4-2-2 Melting Behaviour Following Non-Isothermal Crystallisation[3, 8, 9]

The first melting endotherms of PEEK were reported by Blundell and Osborn.[3] Endothermic peaks shown in their paper are not identical to those shown in this study; this is unsurprising as small variations in molecular microstructure, molecular mass distribution and the presence of additives may significantly affect the phase transition kinetics. Therefore, as previously discussed it is important to perform precise determinations of crystallisation kinetics of each polymer system, even within a single batch.

DSC thermograms of the re-heating cycle, following non-isothermal crystallisation, of the neat PEEK, PEEK + 3 % nanographite and PEEK + 10 % nanographite can be seen in Figure 3-14, Figure 3-15 and Figure 3-16, respectively. The traces are characterised by two melting processes. There is a smaller, low-temperature process, and a larger peak that occurs at a well-defined temperature. The lower peak has been attributed to the melting of crystalline regions formed during the previous crystallisation. It is characteristic of the majority of the crystals present in the sample at room temperature, prior to the start of the re-heat run. As the scan progresses it has been proposed that the polymer is going through continually competing re-crystallisation and melting processes. Considering the 1°C min^{-1} PEEK scan it can be seen that the onset occurs at a temperature of 295°C. As the heating rate increases the peak moves to lower temperatures and becomes much more diffuse. This is most likely due to the fact that under higher cooling rates the molecules are forced to crystallize in a much shorter time, resulting in less perfection of the crystals and a lower level of crystallinity. If the nanomaterial is seeding the crystal growth a higher level of nucleation will lead to a larger number of growth centers which will interact with one another earlier in the crystallisation process.

The upper, more defined peak is caused by the competing effects discussed in the previous paragraph; the temperature of this main melt peak is hardly affected by the addition of the nanographite, with the melting point at 345°C at 1°C min^{-1} for the neat PEEK, and 346°C in the case of 10 % nanographite polymer blend. This peak is representative of the polymer system. The lower melting point peak is seen to become more diffuse and shift to lower temperatures, in all cases, as the cooling rate increases.

It should be noted that the melting points reported here are approximately 10°C higher than those reported by Blundell and Osborn,[3] who reported a well defined melting process at ~335°C. The disparity could be due to the different crystallisation conditions – a slightly higher melting point is found accompanying a higher crystallisation temperature – or it may be the result of a different molar mass distribution arising from the synthesis procedure, in our case.

Table 3-4 - Cooling rate, $T_{(CC)}$, T_m and ΔH_{cryst} values for PEEK, PEEK + 3 % nanographite and PEEK + 10 % nanographite

Sample	Cooling rate (°C min^{-1})	$T_{(cc)}$ (°C)	T_m (°C)	ΔH_{cryst} (J g $^{-1}$)	Corrected Crystallinity (%)
PEEK	1	314±0.5	345±0.5	68.3±3.4	52.5±2.6
	2	306±0.5	344±0.5	56.2±2.8	43.2±2.2
	3	305±0.5	343±0.5	68.0±3.4	52.3±2.6
	4	308±0.5	342±0.5	62.7±3.1	48.2±2.4
	5	297±0.5	343±0.5	62.3±3.1	47.9±2.4
	7	296±0.5	342±0.5	65.1±3.3	50.1±2.5
	10	292±0.5	342±0.5	62.3±3.1	47.9±2.4
	20	284±0.5	342±0.5	56.8±2.8	43.7±2.2
	40	277±0.5	342±0.5	54.5±2.7	41.9±2.1
	80	264±0.5	343±0.5	52.6±2.6	40.5±2.0
PEEK + 3 % nanographite	1	318±0.5	346±0.5	66.2±3.3	52.3±2.6
	2	314±0.5	344±0.5	61.0±3.1	48.4±2.4
	3	312±0.5	344±0.5	65.6±3.3	52.0±2.6
	5	309±0.5	343±0.5	59.8±3.0	47.4±2.4
	7	306±0.5	343±0.5	63.5±3.2	50.4±2.5
	10	303±0.5	343±0.5	58.7±2.9	46.6±2.3
	20	297±0.5	342±0.5	54.3±2.7	43.1±2.2
	40	289±0.5	341±0.5	52.3±2.6	41.5±2.1
	80	290±0.5	341±0.5	48.1±2.4	38.1±1.9
PEEK + 10 % nanographite	1	321±0.5	346±0.5	59.0±3.0	50.4±2.5
	2	317±0.5	345±0.5	59.4±3.0	50.8±2.5
	5	312±0.5	344±0.5	58.6±2.9	50.1±2.5
	10	307±0.5	344±0.5	56.0±2.8	47.9±2.4
	20	302±0.5	342±0.5	54.6±2.7	46.7±2.3
	40	297±0.5	342±0.5	50.7±2.5	43.3±2.2
	80	290±0.5	342±0.5	44.4±2.2	37.9±1.9

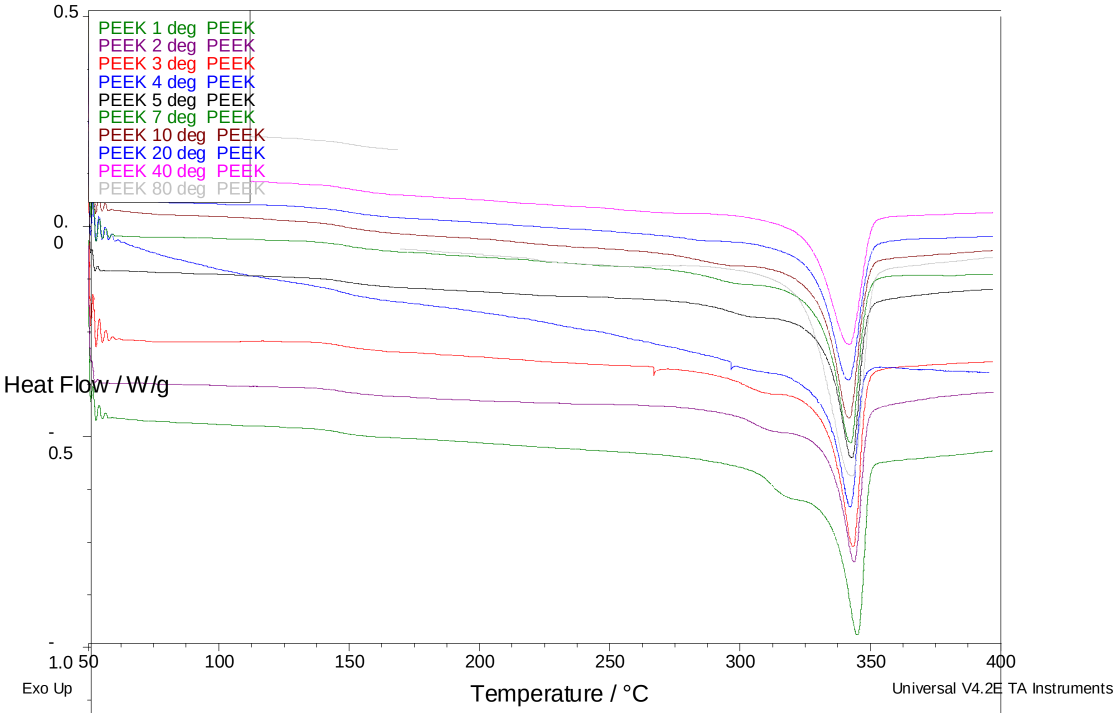

Figure 3-14 Overlaid DSC reheat curves of PEEK

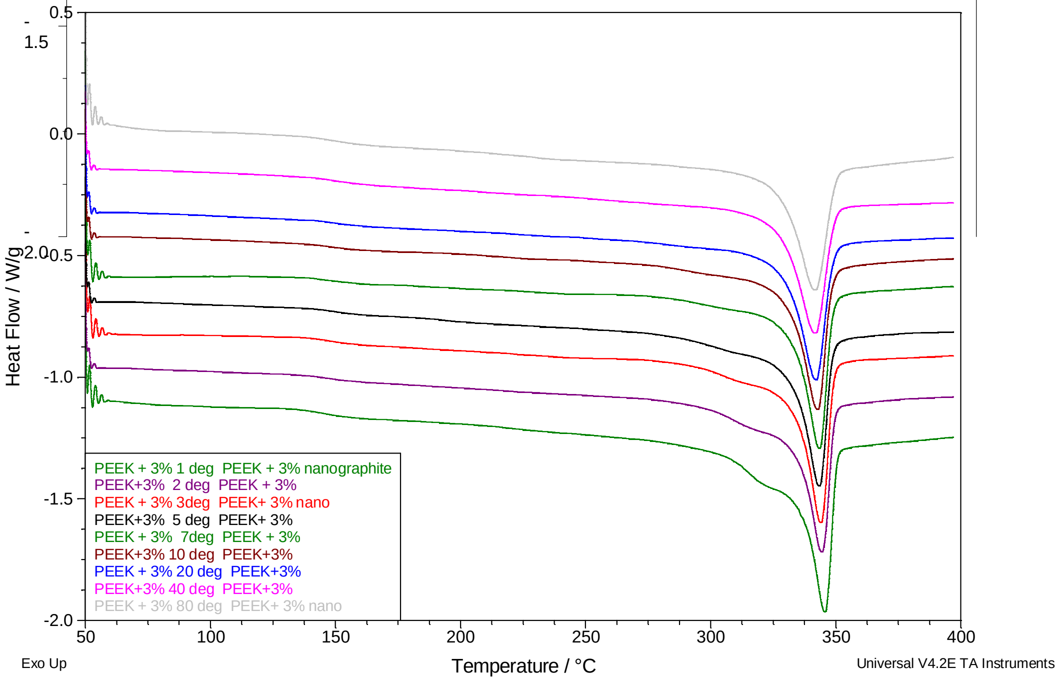

Figure 3-15– Overlaid DSC reheat curves of PEEK + 3 % nanographite

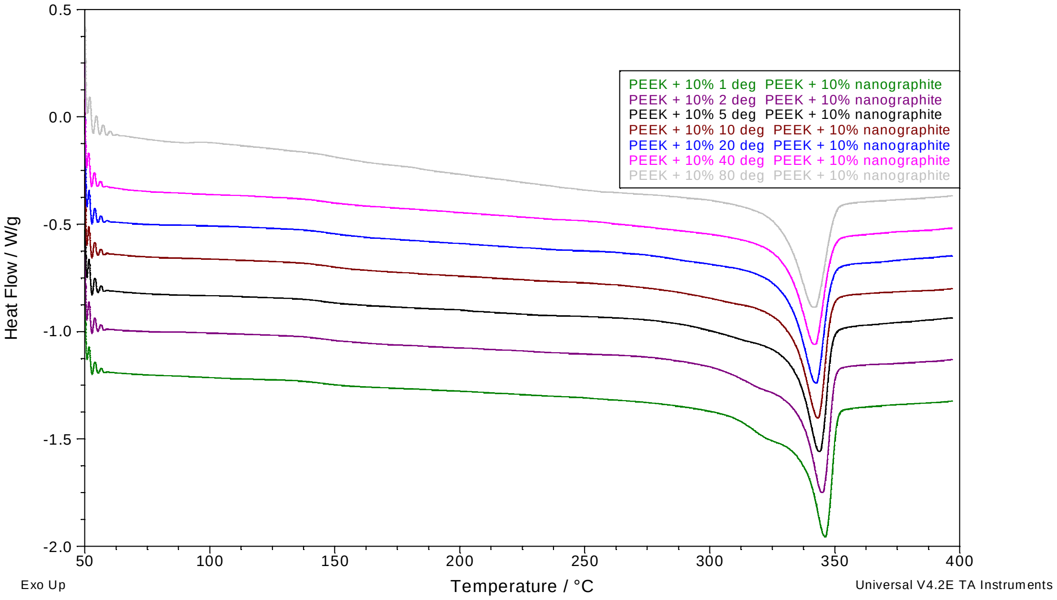

Figure 3-16 - Overlaid DSC reheat curves of PEEK + 10 % nanographite

Stepwise integration of the exothermic peaks during the non-isothermal scans gives the relative degree of crystallinity as a function of temperature. In order to determine rate dependent kinetics of the crystallisation process the temperature curves must be converted to time. This was possible by using Equation 2-9. The onset of crystallisation, T_{onset}, is determined for each cooling rate from the original spreadsheet data, see Table 3-5. Resultant plots of % fractional crystallinity vs. temperature are displayed in Figure 3-17, Figure 3-18, and Figure 3-19.

When one considers the shape of the curves, it is always S-shaped, indicating a two-step crystallisation process is occurring, where there is a fast ‘primary’ stage occurring during the early stages of the crystallisation, closely followed by a slower ‘secondary’ process occurring as the crystallisation moves through to completion. The inflection point, t_i, in each curve represents the temperature corresponding to the maximum rate of heat flow and, in all cases, is taken from the temperature value at a relative crystallinity value of 50 % -T_{50}. It can be seen from Table 3-5 that as the cooling rate increases the temperature of the inflection point decreases i.e. in the case of PEEK the inflection point occurs at 312.6°C in 12.4 minutes for the 1°C min^{-1} run, compared to 265°C and 0.4 minutes when one considers the 80°C min^{-1} run. It must be stated at this point that the error associated with the time at the very high cooling rates is extremely high; in this case the error associated with the 80°C cooling rate is 0.5 minutes, which is actually larger than the time, which is 0.4 minutes.

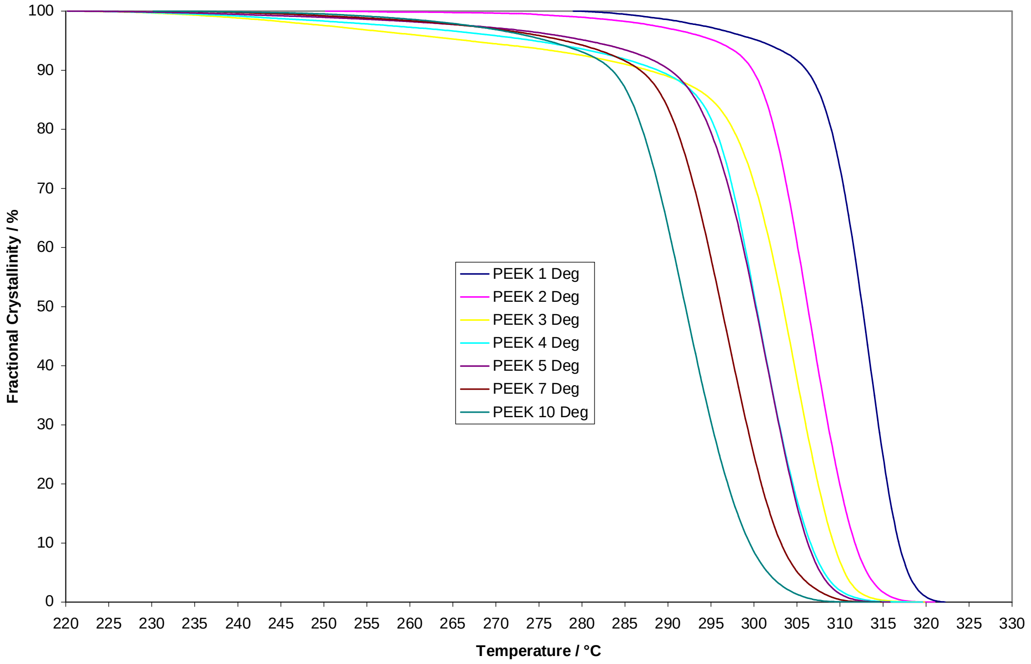

Figure 3-17 – Relative crystallinity versus temperature during non-isothermal crystallisation at the indicated cooling rates for PEEK

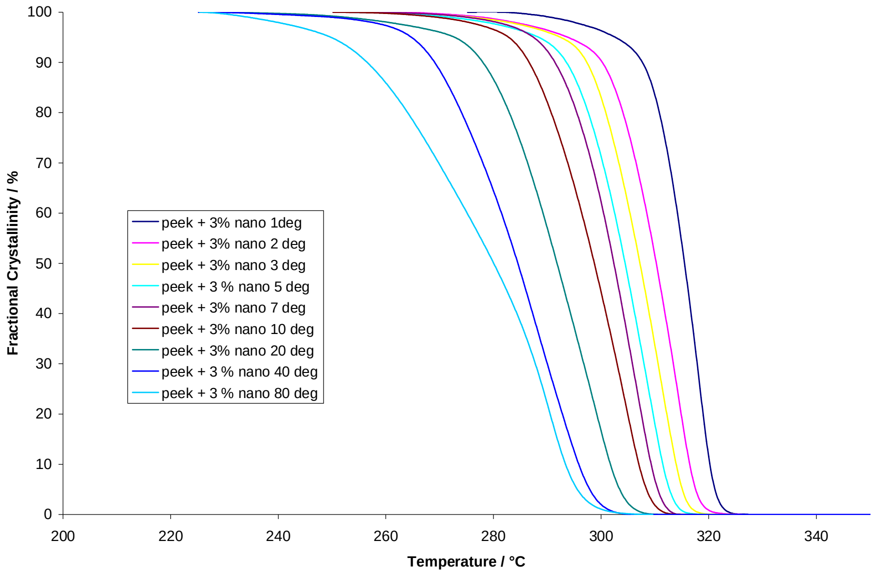

Figure 3-18 – Relative crystallinity versus temperature during non-isothermal crystallisation at the indicated cooling rates for PEEK + 3 % nanographite

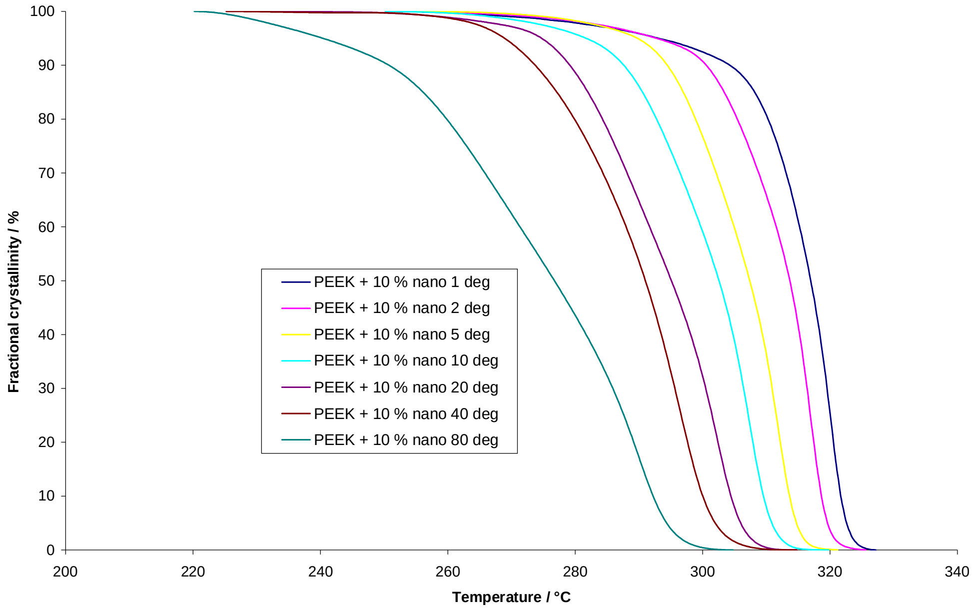

Figure 3-19 –- Relative crystallinity versus temperature during non-isothermal crystallisation at the indicated cooling rates for PEEK + 10 % nanographite

Table 3-5 – Cooling rate, T_{onset}, T_{50} and Time values for PEEK, PEEK + 3 % nanographite and PEEK + 10 % nanographite

Sample	Cooling rate (°C min^{-1})	T_{onset} (°C)	T_{50} (°C)	Time, t_i (mins)
PEEK	1	325±0.5	312.6±0.5	12.4±0.5
	2	325±0.5	306.2±0.5	9.4±0.5
	3	320±0.5	303.4±0.5	5.5±0.5
	4	320±0.5	300.2±0.5	5.0±0.5
	5	315±0.5	300.2±0.5	3.0±0.5
	7	315±0.5	296.2±0.5	2.7±0.5
	10	315±0.5	292.2±0.5	2.3±0.5
	20	310±0.5	285.0±0.5	1.3±0.5
	40	305±0.5	276.8±0.5	0.7±0.5
	80	300±0.5	265.0±0.5	0.4±0.5
PEEK + 3 % nanographite	1	328±0.5	315.6±0.5	12.4±0.5
	2	327±0.5	310.2±0.5	8.4±0.5
	3	325±0.5	307.2±0.5	5.9±0.5
	5	320±0.5	304.4±0.5	3.1±0.5
	7	315±0.5	302.4±0.5	1.8±0.5
	10	315±0.5	298.8±0.5	1.6±0.5
	20	315±0.5	291.8±0.5	1.2±0.5
	40	310±0.5	284.6±0.5	0.6±0.5
	80	310±0.5	280.2±0.5	0.4±0.5
PEEK + 10 % nanographite	1	330±0.5	317.0±0.5	13±0.5
	2	330±0.5	313.6±0.5	8.2±0.5
	5	320±0.5	307.4±0.5	2.5±0.5
	10	320±0.5	302.6±0.5	1.7±0.5
	20	315±0.5	295.2±0.5	1.0±0.5
	40	315±0.5	291.0±0.5	0.6±0.5
	80	305±0.5	276.8±0.5	0.4±0.5

3-4-2-3 Modified Avrami Model

Isothermal crystallisation kinetics of a polymer system is generally analysed using the Avrami equation. However, theoretical analysis of non-isothermal crystallisation is more complicated. As discussed in Section 2-2, the primary stage of non-isothermal crystallisation can still be described by the Avrami equation with the assumption that the crystallisation temperature remains constant with a constant cooling rate.

In order to apply the Avrami equation to the non-isothermal data the crystallisation time must first be obtained using Equation 2.9. Linear fits of the relative crystallinity between values of 3-50 % can then be plotted in order to get an insight into the primary crystallisation behaviour. This region was utilised in order to look at the analysis at the initial crystallisation stages without the addition of any complicated spherulitic impingement effects. The resultant graph can be seen in Figure 3-20. In addition, a Table with information from the graph is shown as Table 3-6. The Avrami constant, n, is known to describe the growth mechanism and geometry of the crystallisation. From the table it can be seen that irrespective of whether the material is neat PEEK or a nanoparticle containing sample, the value of n decreases with increasing cooling rates. This suggests that, at the higher cooling rates the nucleation mechanism is less complicated, as the time available to crystallize decreases.

It was seen in Section 3.4.2.1 that the crystallisation temperature of the polymer was increased significantly by the addition of the nanographite. This would lead to an increase in the n values obtained. As can be seen from Table 3-6, the n values of the PEEK nanocomposites are not necessarily higher than those of the corresponding neat PEEK samples, although the highest value obtained was 6.04 for PEEK + 10 % nanographite at a cooling rate of 2°C min^{-1}. This is in contrast to a study carried out by Weng *et al.*[10] who observed that n was lowered significantly in a nylon 6 matrix. In this study the disparity in the reported n values is most likely due to non-representative sampling in the case of the nanographite containing samples. It would be interesting to carry out further measurements in this area in order to be certain, and this will represent an area of further work to be carried out.

Also detailed in Table 3-6 are the values of Z_c, which describes the rate of growth under the non-isothermal conditions. It can be seen from the table that for the same cooling rate, the Z_c values for the nanographite containing samples are higher than those of the neat PEEK. This difference is even more significant for the 3 % sample, which has a Z_c value of 1.0 at 20°C min^{-1} and a value of 6.8 at 2°C min^{-1}. This anomalous result may be a consequence of inhomogeneous mixing, leading to non-representative sampling, with a higher than expected mass of nanographite present in this particular sample. This is, in turn leading to a higher than expected Z_c value.

When considering the pure PEEK at a cooling rate of 2°C min^{-1} it was seen that values of n and Z_c obtained were comparable to a study carried out by Kuo *et al.*[11], who were working at a similar cooling rate of 2.5°C min^{-1}. The n value reported in their study is 6.3, which is similar to the value of 5.8 reported here. The Z_c reported here is 1.3×10^3 min°C $^{-1}$, which is again not dissimilar to their reported value of 2.1×10^3 min°C $^{-1}$.

It should be concluded that generally speaking poor experimental fits were obtained in this analysis, both for the pure polymer and the materials containing nanographite. Thus indicating that this analysis is unable to accurately describe not only the simple crystallization process but also that which occurs when the nanographite may be expected to exert an influence upon the nucleation of crystal growth.

Table 3-6 – The Avrami constant, *n*, and the growth rate constant, Z_c, of crystallisation for PEEK, PEEK + 3 % nanographite and PEEK + 10 % nanographite under non-isothermal crystallisation conditions

Sample	Cooling Rate (°C min^{-1})	*n*	Z_c x 10^3 (min°C $^{-1}$)
PEEK	2	5.8±0.3	1.3±0.07
	20	3.6±0.2	0.9±0.05
PEEK + 3 % nanographite	2	4.6±0.2	6.8±0.3
	20	3.8±0.2	1.0±0.05
PEEK + 10 % nanographite	2	6.0±0.3	1.7±0.09
	20	1.9±0.1	1.1±0.06

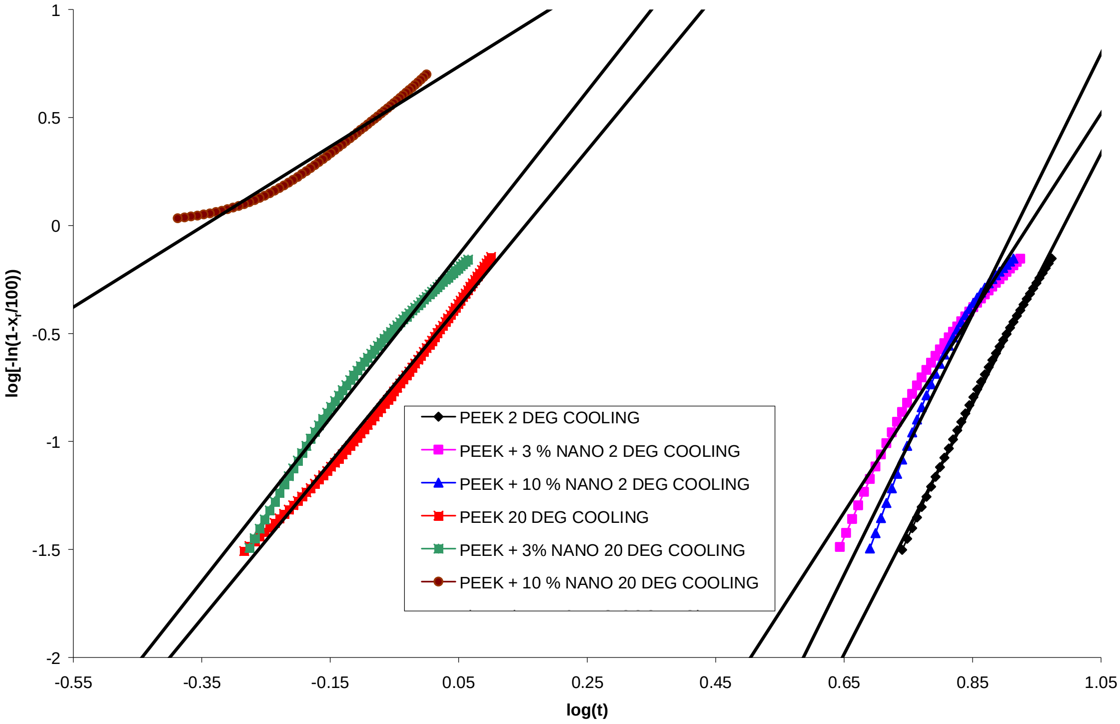

Figure 3-20 – Avrami plot of log[-ln(1-x_r(*t*))] vs. log(*t*) for non-isothermal crystallisation

3-4-2-4 Ozawa Analysis

In order to further discuss and analyse the non-isothermal data the Ozawa analysis was employed. A detailed discussion with relevant equations and theory pertaining to the analysis is discussed in Section 2-2-2. Resultant graphs are shown in Figure 3-21, Figure 3.22 and Figure 3-23. If an Ozawa treatment is successful in modeling the data, the resultant plot should give a series of parallel, straight lines. As can be seen in these figures there is a distinct curvature to the lines indicating that the Ozawa model does not accurately fit this data. This has been attributed to a secondary crystallisation process occurring,[2] which has been seen to contribute 45-70 % of the total crystallinity developed.[2] The resultant curves are very similar to those obtained by Kuo *et al.*[11]. As the Ozawa model is based on isothermal crystallisation conditions, by applying it under non-isothermal conditions the rate of crystallisation is now a function of both time and cooling rates. Another major assumption with the Ozawa model is that it assumes a constant cooling function over the crystallisation process. As discussed in the accompanying theory chapter (Section 2-2-2) the cooling function is related to the overall crystallisation rate, and indicates how fast crystallisation occurs.

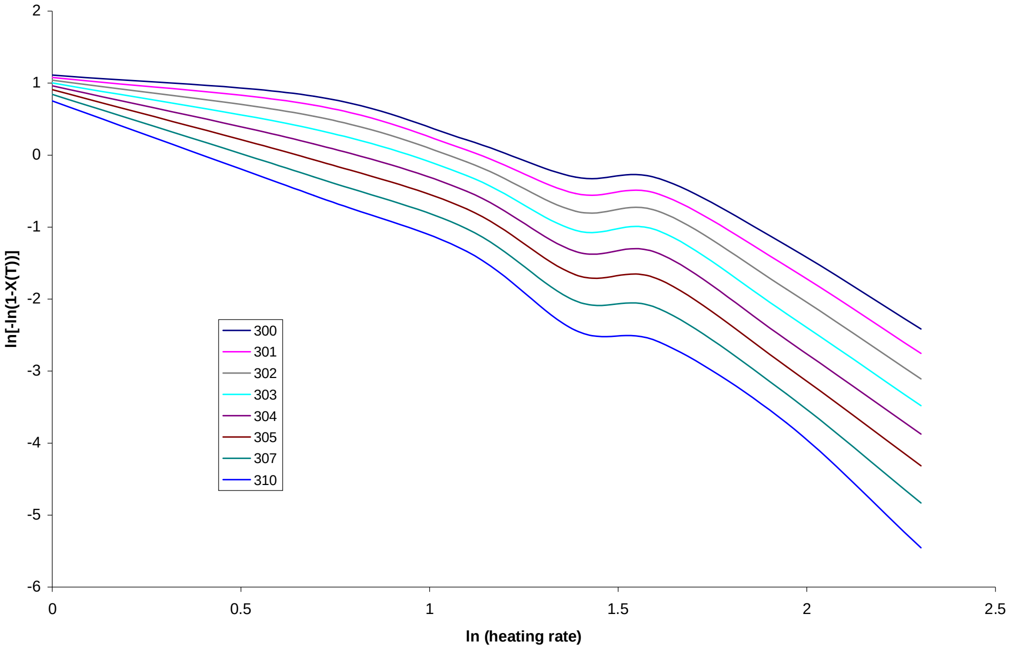

Figure 3-21– Ozawa plot for PEEK

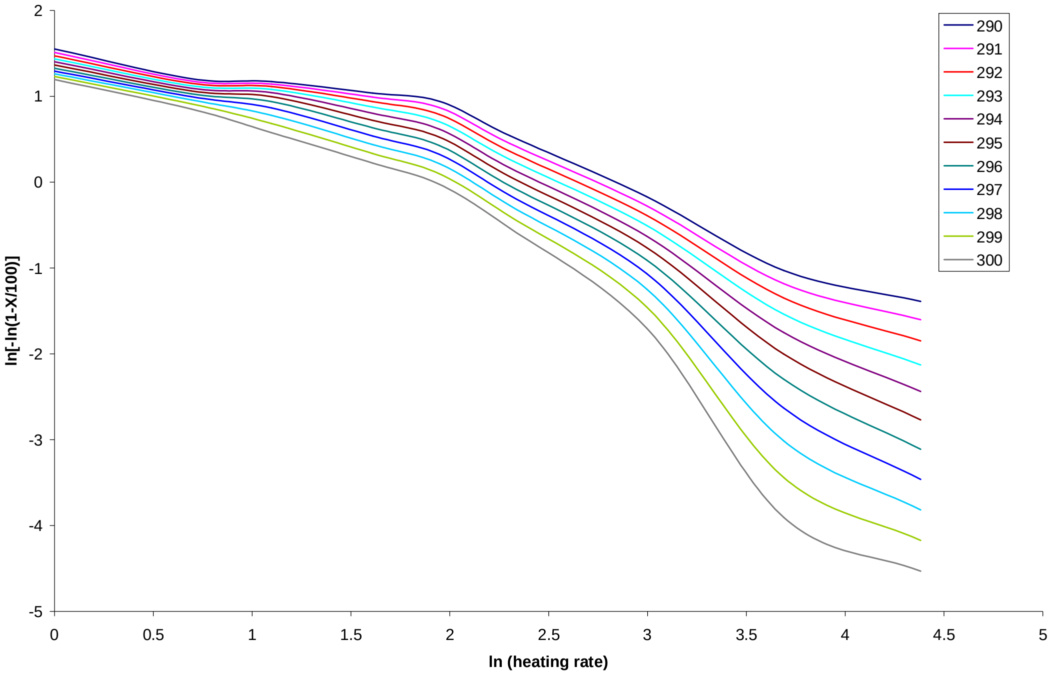

Figure 3-22 – Ozawa plot for PEEK + 3 % nanographite

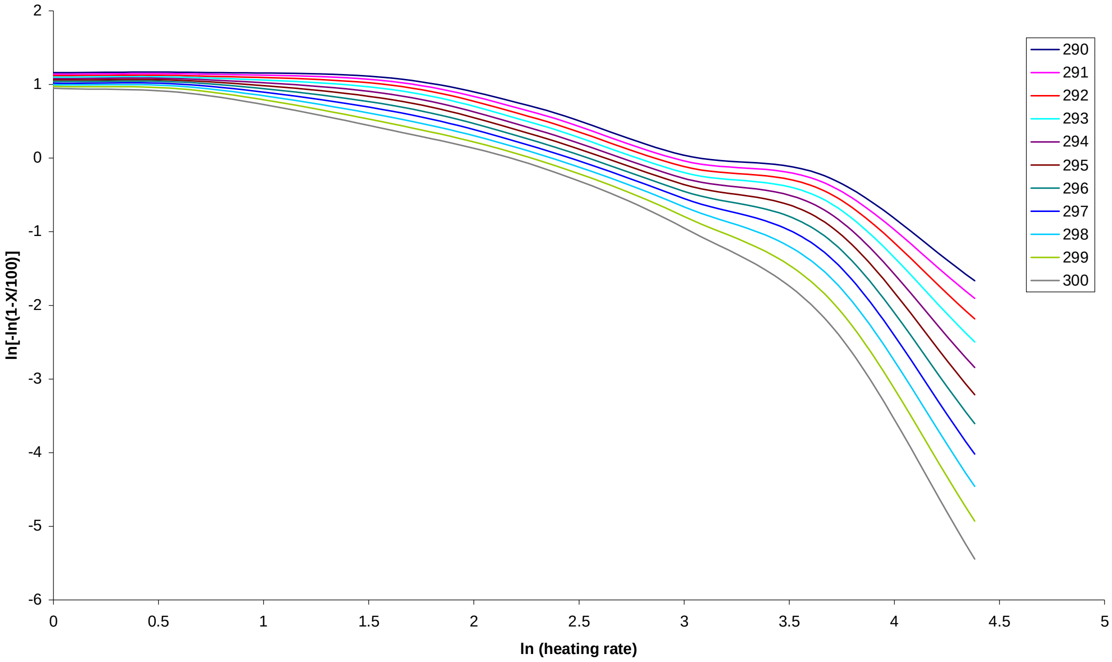

Figure 3-23– Ozawa plot for PEEK + 10 % nanographite

3-4-2-5 Combined Ozawa/Avrami Model

It has been seen that neither the modified Avrami analysis nor the Ozawa analysis have been able to fully describe the crystallisation behaviour of the PEEK and nanographite/PEEK blended polymer systems. In order to further explore the non-isothermal crystallisation, a combined Ozawa/Avrami analysis was applied. The theory and equations pertaining to the model have previously been discussed in Section 2-2-3, where it was seen that a plot of log(a) against log(t), for a fixed level of crystallinity, should give a linear relationship, with intercept of log $F(T)$ and a slope of $-b$. As in the Avrami model applied in Section 3-4-1, the temperatures must initially be converted into time, using Equation 2.9.

As shown in Figure 3-24, Figure 3-25 and Figure 3-26, plots of log(a) vs. log(t), for a fixed level of relative crystallinity, give good linearity, with values of $F(T)$ and b listed in Table 3-7. It can be seen that the values of $F(T)$ increase systematically with increasing relative crystallinity. This indicates that at a unit crystallisation time, a higher cooling rate is needed to achieve a higher degree of crystallinity. Corresponding $F(T)$ values for the composites are larger than for the neat PEEK – though values for both the 3 % and 10 % loadings are very similar – indicating that the crystallisation rate is higher for these materials than the neat PEEK. The values of b show only a small increase over the range of the experiment. In a similar study carried out by Kuo *et al.* [11] the value of b reported for 20 % crystallinity of PEEK was 1.2; compared with a value of 0.8 obtained in this study. For the same level of crystallinity, the value of $F(T)$ reported was 6.9, which is lower than the 10.3 value reported in this study. Again differences are attributed to differences in synthesis and also to any small variations in molecular microstructure, molecular mass distribution or the presence of additives, which may significantly affect the reaction kinetics reported.

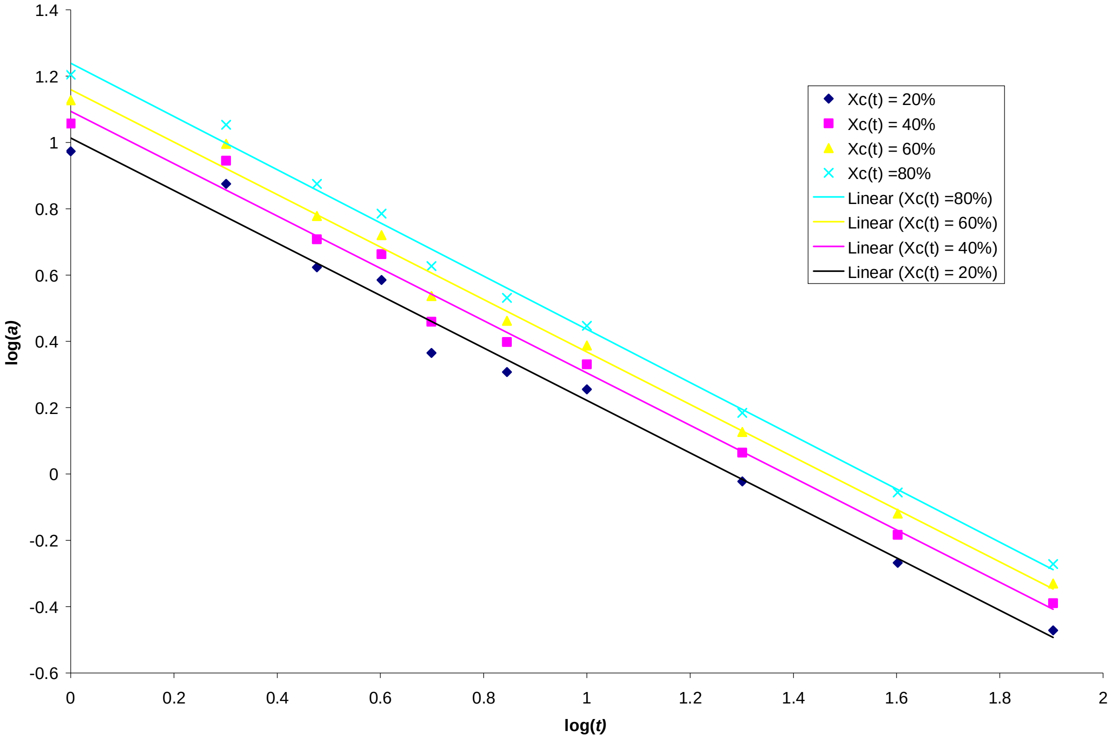

Figure 3-24 - Combined Ozawa Avrami plot for PEEK

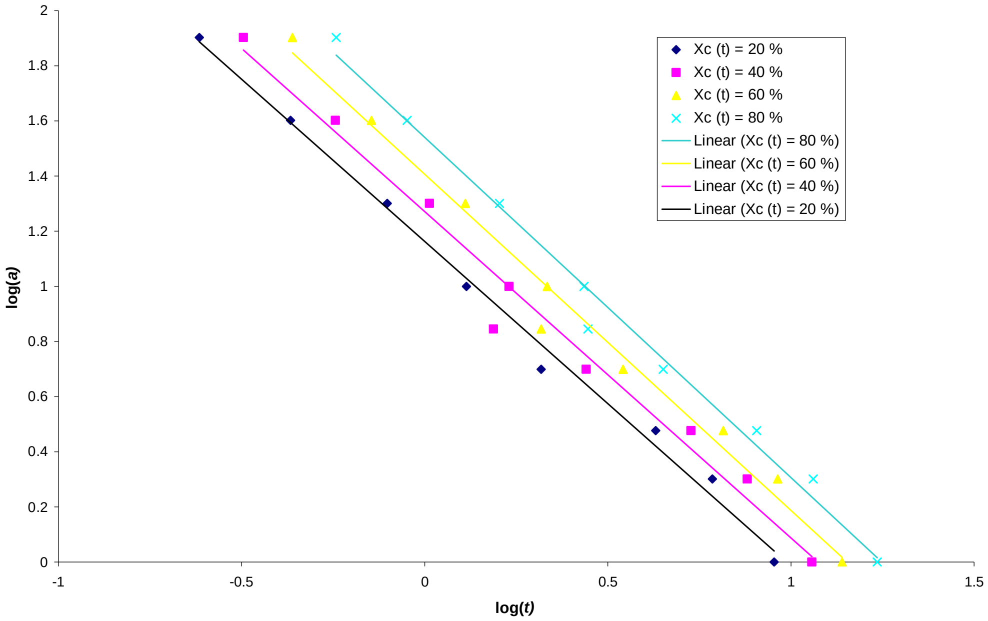

Figure 3-25 - Combined Ozawa Avrami plot for PEEK + 3 % Nanographite

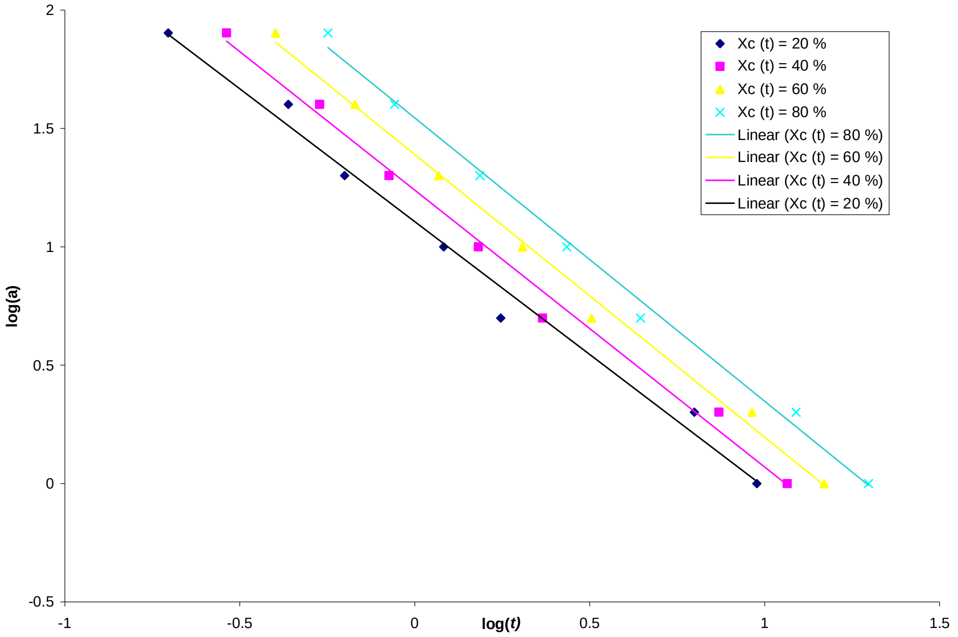

Figure 3-26 - Combined Ozawa Avrami plot for PEEK + 10 % Nanographite

Table 3-7 Avrami-Ozawa parameters of the PEEK, PEEK + 3 % nanographite and PEEK + 10 % nanographite material

		20 % Crystallinity	**40 % Crystallinity**	**60 % Crystallinity**	**80 % Crystallinity**
PEEK	***F(T)***	10.3±1.0	12.4±1.2	14.4±1.4	17.3±1.7
	b	0.8±0.08	0.8±0.08	0.8±0.08	0.8±0.08
PEEK + 3 % nanographite	***F(T)***	14.6±1.5	18.7±1.9	25.5±2.6	34.7±3.5
	b	1.2±0.1	1.2±0.1	1.2±0.1	1.2±0.1
PEEK + 10 % nanographite	***F(T)***	12.8±1.3	17.4±1.7	24.5±2.5	35.0±3.5
	b	1.1±0.1	1.2±0.1	1.2±0.1	1.2±0.1

3-4-2-6 Maximum Rate of Crystallisation

The maximum level of crystallisation *dx/dt* was calculated for each polymer system, and a table was constructed showing the temperature and the cooling rate for each system, see Table 3-8. It can be seen from the table, that in each case, the maximum level of crystallisation increases as the cooling rate increases, which would be expected. It can also be seen that the maximum level of crystallisation occurs at a lower temperature upon increasing cooling rate. Again, this would be expected and thus introduces an additional level of confidence in the results being presented in this study.

Table 3-8 – Table showing maximum level of crystallisation, cooling rate and temperature for each polymer system

Sample	Cooling rate (°C) min^{-1}	*dx/dt* (min^{-1})	Temperature (°C)
PEEK	1	0.11	312.8±0.5
	2	0.18	305.8±0.5
	3	0.24	304.8±0.5
	4	0.31	299.8±0.5
	5	0.37	300.8±0.5
	7	0.47	299.8±0.5
	10	0.68	291.8±0.5
PEEK + 3 % nanographite	1	0.09	317.8±0.5
	2	0.14	313.8±0.5
	3	0.18	310.8±0.5
	5	0.30	308.8±0.5
	7	0.48	305.8±0.5
	10	0.51	303.8±0.5
	20	0.83	298.8±0.5
	40	1.48	287.8±0.5
PEEK + 10 % nanographite	1	0.10	319.8±0.5
	2	0.19	316.8±0.5
	5	0.39	311.8±0.5
	10	0.69	306.8±0.5
	20	1.08	301.8±0.5
	40	2.02	295.8±0.5

3-5 Conclusions

The investigation of the isothermal and non-isothermal crystallisation kinetics of neat PEEK, PEEK +3 % nanographite and PEEK + 10 % nanographite polymer systems was carried out using differential scanning calorimetry. It is stated at this point that the numerical results quoted in this chapter do not lend themselves to be absolute and it is stated that the general trends only can be taken from the data. Having said that it was observed that under isothermal conditions the time to reach maximum crystallinity decreased with the introduction of increasing quantities of nanographite, thus indicating a significant nucleating effect of the nanographite upon the PEEK. The Avrami equation was used to analyse the isothermal crystallisation of the samples. From this part of the study it was seen that the equation was able to describe the kinetics of the reaction well. The Avrami exponent for the neat PEEK was found to be ~3.5, which is consistent with heterogeneous nucleation and three dimensional spherulitic growth. With the introduction of the nanographite, the Avrami exponent moved to slightly lower values, typically in the region of 1-2, which indicates a shift in the crystallisation kinetics involved. The variation in n was reported to be due to inhomogeneity of sampling.

In the case of non-isothermal crystallisation it was seen that, for all polymer systems, the value of the crystallisation exotherm peak shifted to lower temperatures as the cooling rate increased, and the crystallisation temperature of the polymer was increased significantly by the addition of the nanographite. This is again showing the ability of the nanographite to act as a nucleating agent. In the case of the PEEK isothermal crystallisation curves, a single symmetrical exothermic peak was reported. With the addition of the nanographite, it was seen that the curves became asymmetric, indicating that the crystallisation kinetics are becoming more complex. This was reported to be due to a combination of factors; the dominant effects of different crystallisation mechanisms occurring in the presence of nanographite; the multiple exothermic peaks potentially arising from phase-separated components, where crystallisation is delayed in the remaining heterogeneity-free domains. It may also be that inhomogeneity of sampling is adding to the complexity of the crystallisation mechanisms.

The modified Avrami equation and the Ozawa equation were applied and were found to be inadequate in fully describing the crystallisation kinetics of the systems. This was most likely due to the occurrence of a secondary crystallisation process occurring and the inaccurate assumption of a constant cooling function over the crystallisation process. The combined Avrami/Ozawa equation was then utilised and was found to be more effective in describing the reaction kinetics, with plots of log(*a)* against log(*t)* giving good linearity. It was seen that the rate of crystallisation was slower in the case of the nanographite containing samples than the neat PEEK. In conclusion the maximum rate of crystallisation was calculated for each polymer system at each cooling rate. It was seen that results fitted well with expectations and therefore introduced an additional level of confidence in the results being presented in this study.

This study has proven highly interesting with results indicating that if nanographite were present in a PEEK sample which was subsequently processed in an extruder, there is a high probability that an enhanced rate of crystallisation would occur. As such, consequential effects on the processability of the materials would no doubt be experienced. This may translate as effects upon the resultant conductivity of the composite, and further work must involve determining if the nucleating effect of the nanographite has a stronger effect on the percolation threshold of the nanocomposites than the aspect ratio, as was reported in a study carried out by Kalaitzidou *et al*.[1]

3-6 References

1. K. Kalaitzidou, H. Fukushima, P. Askeland, L.T. Drzal, *The nucleating effect of exfoliated graphite nanoplatelets and their influence on the crystal structure and electrical conductivity of polypropylene nanocomposites.* Journal of Materials Science, 2007. **43**(8): p. 2895-2907.

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