# CHAPTER 8 CONCLUSIONS

The isothermal and non-isothermal crystallization kinetics of neat PEEK, PEEK + 3 % nanographite and peek + 10 % nanographite polymer systems were studied using DSC. Under isothermal conditions it was seen that the nanographite was having a nucleating effect upon the PEEK, with the Avrami equation describing the kinetics of the reaction well. The Avrami exponent moved to slightly lower values, typically in the region of 1-2, which indicates a shift in the crystallization kinetics involved. The variation in n was reported to be due to inhomogeneity of sampling.

In the case of non-isothermal crystallization it was seen that the crystallization 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. The crystallization kinetics were also seen to become more complex under non-isothermal conditions.

The modified Avrami equation and the Ozawa equation were also applied and were found to be inadequate in fully describing the crystallization kinetics of the systems. This was most likely due to the occurrence of a secondary crystallization process and the inaccurate assumption of a constant cooling function over the crystallization process. The combined Avrami/Ozawa equation was then utilized and was found to be more effective in describing the reaction kinetics with plots of $\log(a)$ against $\log(t)$ giving good linearity. In conclusion, it was observed that results fitted well with expectations and therefore introduced an additional level of confidence in the results presented in this study.

When one considers the rheological results presented in the thesis, it was seen that both the PES based co-polymer and the Radel A-100 material showed a high degree of viscoelasticity, and were also unstable as a consequence of a number of factors: the effects of entanglement, possible further polymerization and transient aggregation in the melt. It is known that close to the melt temperature transient aggregates, enhanced by end group interactions, can be formed which will act rather like entanglements, and these are sensitive to the level of shear stress. It is possible that this may be partly responsible for some of the transient behaviour observed with these materials. In addition there would appear to be rheological variation in samples, which is caused by molecular weight effects and, in the case of PES based co-polymer, the possibility of end group reactions.

These rheological studies indicated potential processing implications may become apparent when considering extrusion as a possible technique. The results also showed the possibility that even fibre flow may not be possible as the polymer goes to a fine thread, with this effect becoming increasingly more apparent with the inclusion of the nanomaterial.

When one considers the results of the conductivity chapter of this thesis, it was seen that a conductivity of 14612 S/m could be achieved when carbon fibre was doped in 3M $HNO_3$. This relatively high conductivity was attributed to topographical reasons with increased surface roughness leading to increased acidic functions in this case.

When one considers the nanomaterial results it was seen that solution blending was found to produce composites which percolate at approximately 8 %, with the highest conductivity associated with the 80 % loading level – $7.4\text{-}9.2 \times 10^2$ S/m. The directly blended material was found to produce powders which percolated at approximately 3 %, with the highest conductivity, again, associated with the 80 % loading level – $1 \times 10^4$ S/m.

A small enhancement in the conductivity was seen with the addition of up to 10wt% nanotubes to a directly blended 10 % nanographite/PES based co-polymer powder. This small enhancement was attributed to the materials coming together in a synergistic manner, with the nanotubes acting as mini wires connecting together the graphite platelets.

Increasing additions of carbon black and phthalocyanine did not effectively enhance the conductivity of the 10% nanographite/PES based co-polymer matrix. It was seen, from SEM images, that the carbon black existed discretely within the matrix. As this material is spherical in shape the aspect ratio is lower than the graphite platelets, and as a consequence, no enhancement effect was observed. Regarding the phthalocyanine, it was observed that the additional doping may be required in order for it to be an effective material.

Overall, the disparity in the levels of conductivity achieved has been attributed to the level of dispersion achieved in each case. In the case of the *in-situ* produced materials, a very effective dispersion of the nanomaterial was produced, which led to the introduction of polymer particles between the nanographite platelets, causing a disruption in the percolation pathway and therefore a loss in the resultant conductivity.

Again, a reasonable dispersion was found when carrying out solution blended work. Also, in this case chloroform was used as a solvent. This chloroform was found to become trapped within the pores of the composites, again, causing a disruption to the percolation pathway.

In the case of the directly blended materials there was no interference with platelet-platelet contacts, and consequently the conductivity was found to be much higher in this case.

An extruder was also utilized to determine how conductive processed materials could be. It was seen that, for the same wt% of nanographite the conductivities of extruded materials were approximately three orders of magnitude less than the blended materials. Again, this was attributed to the effective dispersion and orientation gained in the instrument leading to a subsequent loss in conductivity. Subsequent additions of carbon nanotubes and carbon black failed to enhance the conductivity to any large extent.

Further studies using a Plasti-Corder® and an oven also confirmed that the application of heat was aiding dispersion of the nanographite and causing a subsequent loss in the conductivities possible.

Nanographite was blended with other engineering thermoplastics – namely PEEK and PEKK. It was found that both materials led to a higher conductivity than the PES based co-polymer. The differences were not linked to any physical reasons and were therefore attributable to the presence of ionic impurities within the matrix leading to a higher than expected conductivity.

Interestingly, it was seen that additions of TTF TCNQ were found to rebuild the percolation pathway, by the growing of long needle-like crystals using a slow cooling technique. The conductivities achieved were not of the level of the directly blended materials, but it does serve to prove that it is possible to rebuild a percolation pathway which has been disrupted.

In conclusion, the thesis explained the possibilities of creating highly conductive paths in composite structures using PEEK, PEKK and PES fibres as the way in which the structure would be created. It is important to note that the fibre formation process will induce alignment which is detrimental to the creation of conductive pathways. Appropriate levels of conductivity can be achieved using nanographite, although the organisation of this material to produce a percolating, conductive pathway has yet to be achieved.