Chapter 6

POLYAMIDE-6,12 WITH CARBAZOLE

CONTENTS

6.1 Introduction

This chapter extends the work done on melt blends of polyamide-4,6, polyamide-6 and polyamide-6,9 with carbazole with further work on polyamide-6,12/carbazole melt blends.

The polyamide-6,12 differs from the polyamide-4,6 in that the diamine and/or diacid moieties of the repeat unit are both longer than for the other polyamides. It is an "even-even" polyamide-m,n like polyamide-4,6. It differs from polyamide-6 in that it is a polyamide-m,n rather than a polyamide-n type and from polyamide-6,9 which is an "even-odd" polyamide. These factors influence the ways in which the polyamide can crystallise and its melting temperature. They also affect the flexibility of the polymer chains by having a lower density of amide groups and affect other properties such as the melting temperature which is lower than polyamide-4,6 and polyamide-6 but higher than polyamide-6,9.

Some of the themes seen in the earlier chapters will be shown to recur here. The situation is most like that of the polyamide-6/ and polyamide-6,9/carbazole blends because the polyamide-6,12, like the other two, melts below the carbazole melting temperature. The melt is usually a double melt as the material melts/recrystallises and melts again [48 p. 46].

This combination of materials will be shown, like the polyamide-6 and polyamide-6,9 combinations with carbazole, to lead to a linear reduction in carbazole enthalpy of crystallisation with increasing polyamide content. In this case the concentration for zero carbazole crystallinity will be shown to be near 70% by weight of the polyamide.

6.2 Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) was carried out in order to determine the percentage of carbazole in ampoule samples. Figure 6-1 shows a comparison between the theoretical percentage of polyamide and the actual polyamide concentrations in samples taken from ampoule material.

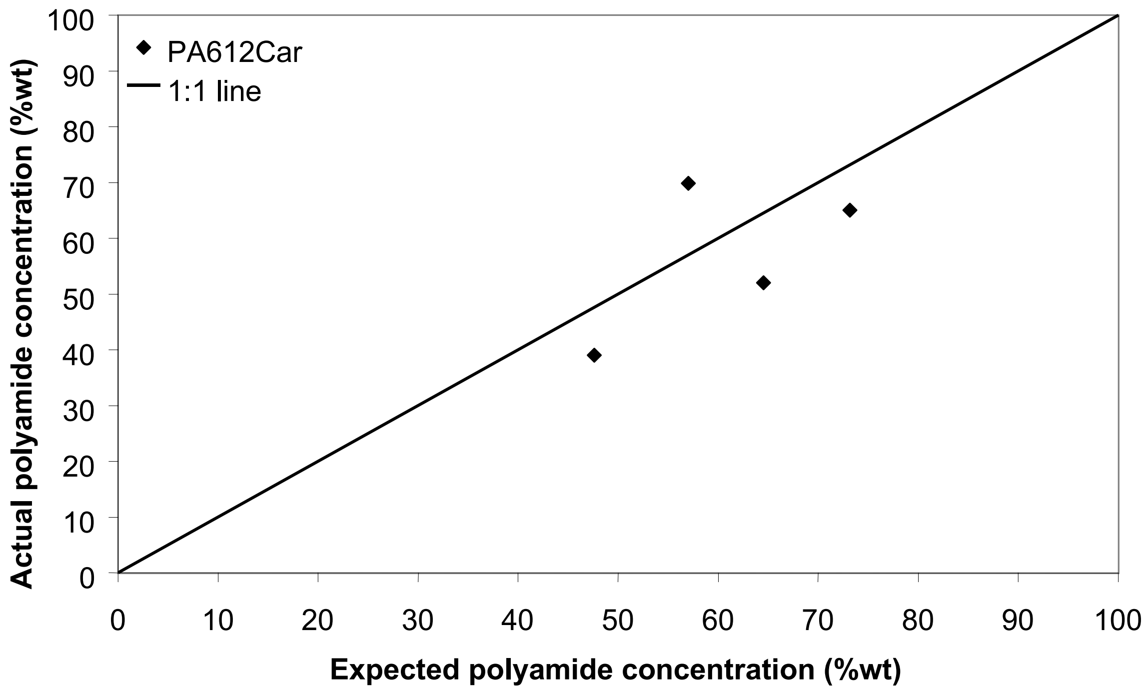

Figure 6-1 Actual versus expected weight percentage polyamide in polyamide-6,12/carbazole samples from ampoules.

Deviations of more than 5% from the expected concentrations of polyamide, as seen in Figure 6-1, are real differences in concentration for the samples compared with the expected. These are variations due to either imperfect mixing in the ampoules or to the way the samples have crystallised in the ampoules.

6.3 Differential Scanning Calorimetry

Polyamide-6,12 has a weak endotherm in the range 170-190 ^{0}C combined with an exotherm at 201 ^{0}C and then a main endothermic peak at 216 ^{0}C The endotherm/exotherm pair is due to the polyamide having crystallised in a metastable form. The metastable form melts above 160 ^{0}C when the sample is heated and recrystallises at 201 ^{0}C into the stable form that melts at 216 ^{0}C. The exotherm between the two endotherms is very conspicuous for this polyamide. The polyamide crystallises at 197 ^{0}C for a cooling rate of 2 ^{0}C/min and at 185 ^{0}C for a cooling rate of 25 ^{0}C/min.

6.3.1 Pan Melt Blending

6.3.1.1 Melting Temperatures for first heating ramp of the powders at 5 ^{0}C/min

The individual thermograms for polyamide-6,12, carbazole and two blends shown in Figure 6-2 are described in more detail below:

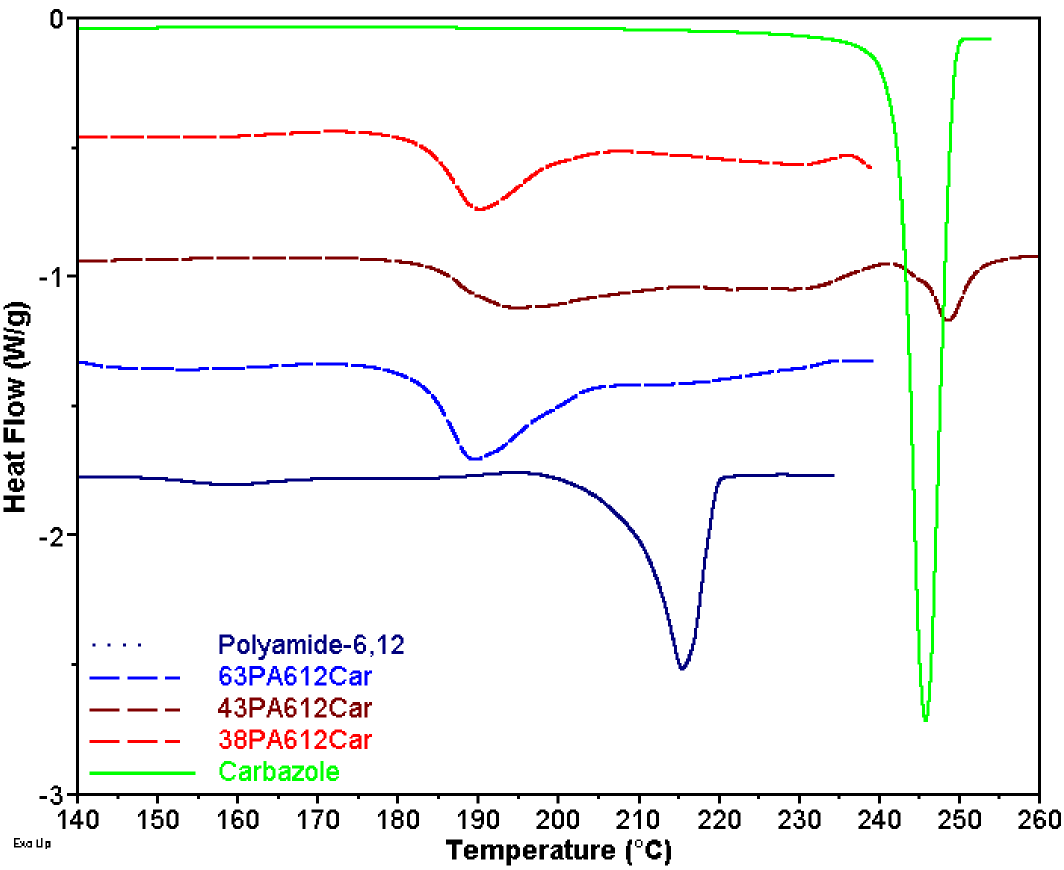

Figure 6-2 DSC thermograms from the first melting at 5 ^{0}C/min of polyamide-6,12 carbazole and powder mixtures.

a) The sample 63PA612Car was formed when polyamide-6,12 began to melt as it dissolved carbazole at the same time. The main endothermic peak is just under 190 ^{0}C and extends to 205 ^{0}C. There is some indeterminate thermal activity above this temperature, with residual carbazole being dissolved at higher temperatures in the saturated solution.

b) The thermogram for 43PA612Car begins with a similar endotherm to 63PA612Car but changes into a TLS peak for carbazole and has a substantial additional peak near the carbazole melting temperature. The last peak is showing that the solution is either entering a high temperature region where a single phase is unfavourable or there are strong kinetic effects slowing down the dissolution of carbazole into the solution.

c) 38PA612Car encountered experimental difficulties with the data at the higher end of the ramp and has been cut short. It also had quite a noticeable loss of carbazole through evaporation. It has, however, been included because it provides supplementary information to the other thermograms and the data from crystallisation and the repeat cycle were good. The thermogram follows a similar path to the previous two samples except that there is more carbazole to dissolve above the main dissolution/melt. The data where the thermogram had to be terminated was clearly taking a path akin to that of the 43PA612Car sample that had a final melting of residual carbazole only at the carbazole melting temperature.

The initial melting of the metastable form of polyamide-6,12 is coupled with the dissolution of carbazole before the polyamide has the chance to recrystallise properly into the metastable form. The relatively large peak for the melting of carbazole at the carbazole melting temperature for 43PA612Car and indications of similar behaviour for 38PA612Car show that there is either a miscibility problem at high temperatures and carbazole concentrations or the kinetics of the dissolution are quite slow.

6.3.1.2 Crystallisation for first cooling ramp of the molten blend at 25 ^{0}C/min

A set of thermograms is seen in Figure 6-3 for the first crystallisation at 25 ^{0}C/min with powders melt-blended in pans.

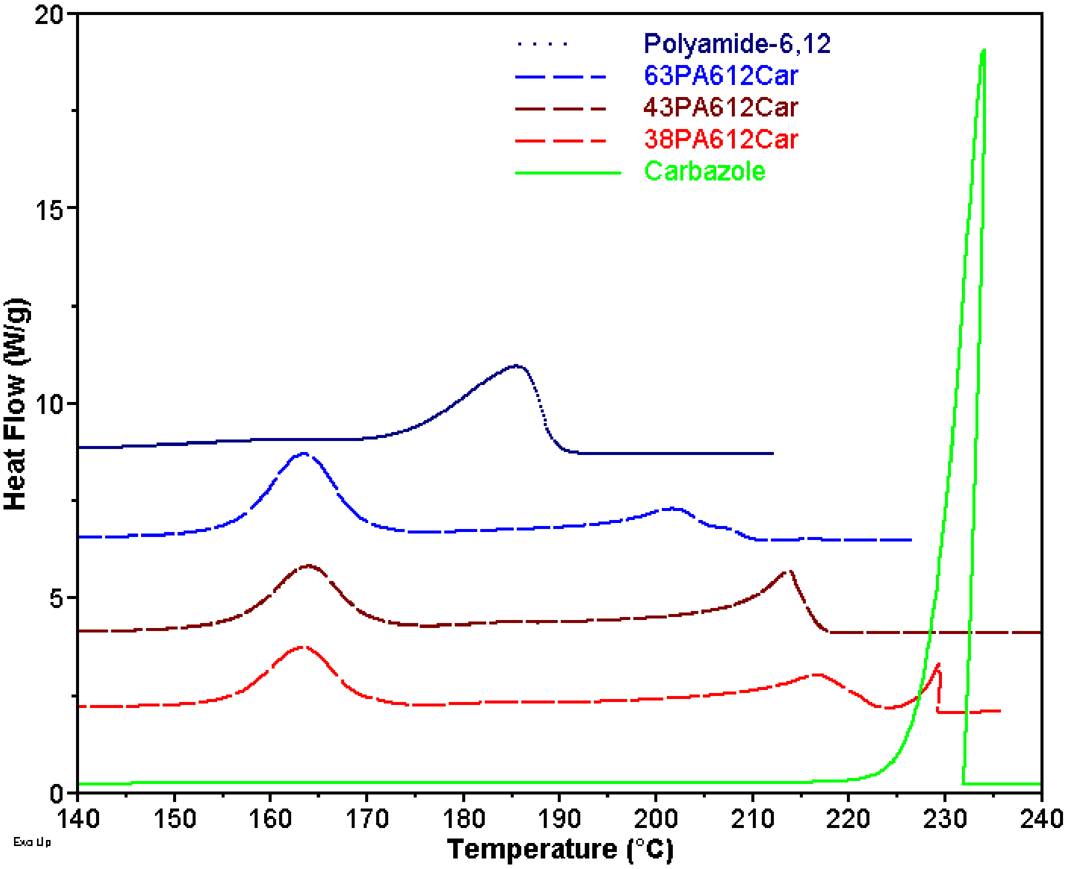

Figure 6-3 DSC thermograms for first crystallisation of pan blended polyamide-6,12/carbazole from the melt at 25 ^{0}C/min.

a) The cooling of the 63PA612Car sample is showing no evidence of separate crystallisation of nearly pure carbazole domains within the liquid but there is crystallisation of, what appears to be, a compound/blend of polyamide-6,12 and carbazole at temperatures well above the normal crystallising temperature of the polyamide. This is followed by the crystallising of polyamide-6,12 with substantial amounts of carbazole depressed more than 20 ^{0}C below the normal crystallising temperature of polyamide-6,12, in the manner seen with other polyamides.

b) The thermogram for 43PA612Car is similar to the above but with the first peak at a higher temperature.

c) The cooling of 38PA612Car begins with a small crystallisation of some carbazole followed by the crystallising of a polyamide-6,12/carbazole blend at higher temperatures than seen above with the 63PA612Car and 43PA612Car samples. The cooling process then results in the crystallising of the remaining polyamide-6,12/carbazole in the sample at an identical temperature and peak shape to the other two blends. There is some phase separation occurring here with the first peak at virtually the same temperature as for pure carbazole. The crystallisation coming from phase separation substantiates the comments made in the previous section on the first melting.

The cooling part of the cycle for the first heat/cool process of polyamide-6,12 and carbazole powders shows behaviour typical of a eutectic phase diagram as will be shown later in the chapter. There is a large peak depressed a constant amount from polyamide-6,12 crystallisation and above that there is a peak which decreases in peak temperature as the amount of carbazole is reduced. The eutectic composition must lie above 63% polyamide because the upper peak for 63PA612Car is above the polyamide-6,12 crystallisation temperature. Additionally, at high temperatures and high carbazole concentrations, there is phase separation taking place.

6.3.1.3 Melting Peak Temperatures for second heating ramp at 5 ^{0}C/min

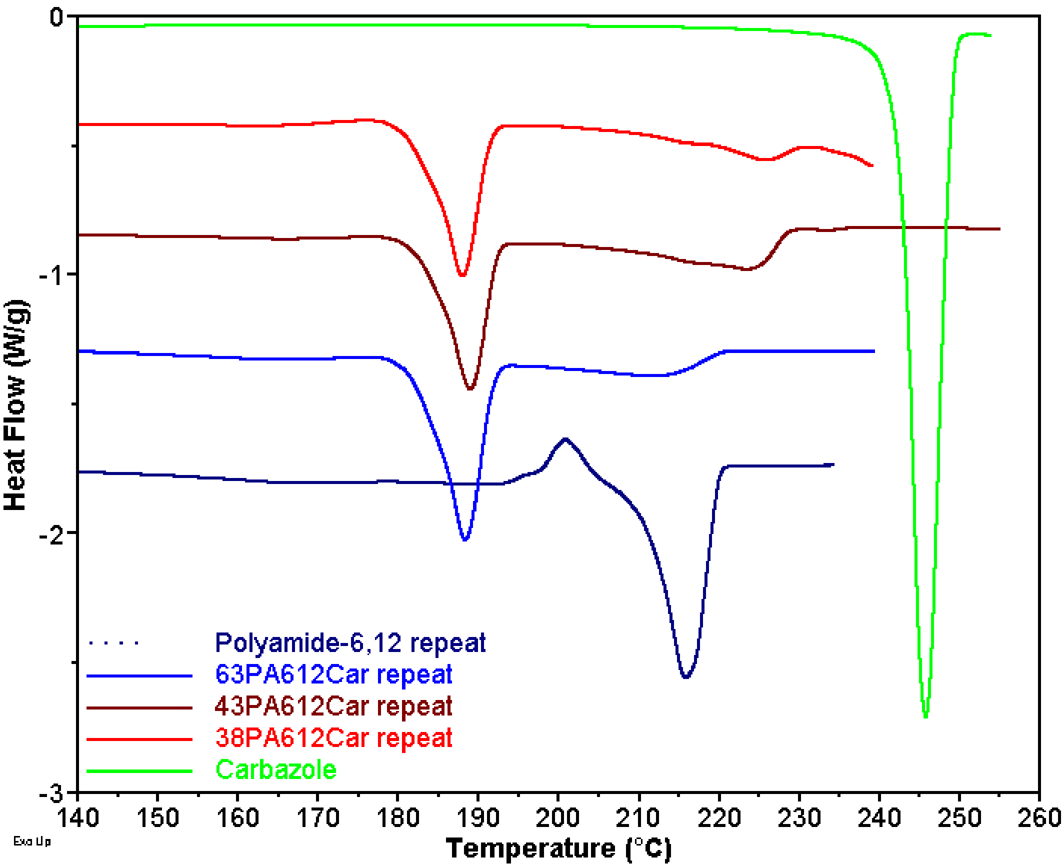

Figure 6-4 DSC thermograms of second melt at 5 ^{0}C/min for materials previously crystallised in pans for polyamide-6,12/carbazole.

The thermograms in Figure 6-4 for the second melting of pan blended samples at 5 ^{0}C/min are slightly different from the first powder melting. This is the same `as in Chapters 3 to 5 where there were differences because the melt is now starting from a closer molecular mixing of the materials.

a) The remelting of polyamide-6,12, known to have crystallised at 25 ^{0}C/min, displays the typical slow melting of the metastable form, the sharp exothermic re-crystallisation at 203 ^{0}C into the stable lamellar form and the main melting of that stable form of the polyamide at 216 ^{0}C.

b) The 63PA612Car sample, on remelting, shows the melting of the carbazole/polyamide depressed by 27 ^{0}C. That melting is displaying only a little evidence of a metastable-to-stable conversion. The lamellae are either in the stable form or are hindered by the carbazole from making the conversion. The main melting peak is followed by the carbazole TLS peak.

c) The thermogram for 43PA612Car is similar to the 63PA612Car sample except that the TLS peak is at higher temperatures.

d) The melting of the previously formed 38PA612Car sample is almost identical for the main peak to that of the 63PA612Car and 43PA612Car samples above. A TLS peak for the remaining carbazole in the saturated solution can be seen. The general fall-off in the thermogram as the temperature raises above the main peak is due to significant carbazole evaporation from the sample. This sample only had 58% of the original carbazole level after the two heating/cooling cycles applied to it as a post-DSC weighing found. Another set of samples near this concentration could possibly have been run on TGA and DSC with another attempt to get good sealing of the hermetic DSC pans.

The common experience of repeat melting of pan blended powders has given rise again to sharper melting curves. The main melting peaks are depressed in eutectic melts from the normal polyamide-6,12 melting temperature and they do not have significant conversion of metastable to stable form.

6.3.1.4 Crystallisation Peak Temperatures for second cooling ramp at 25 ^{0}C/min

Figure 6-5 presents the DSC thermograms of the second crystallisation at 25 ^{0}C/min of materials originally melt blended in the DSC in from the constituent material powders.

a) There has been a change in the crystallisation of the 63PA612Car sample from the first time it was crystallised from the melt. The higher temperature peak is now showing more characteristics of a sharper crystallisation, although it does not yet have the “spiky” characteristic of a near-pure carbazole crystallisation.

b) The thermogram for 43PA612Car is similar to 63PA612Car except that the upper peak is at a higher temperature.

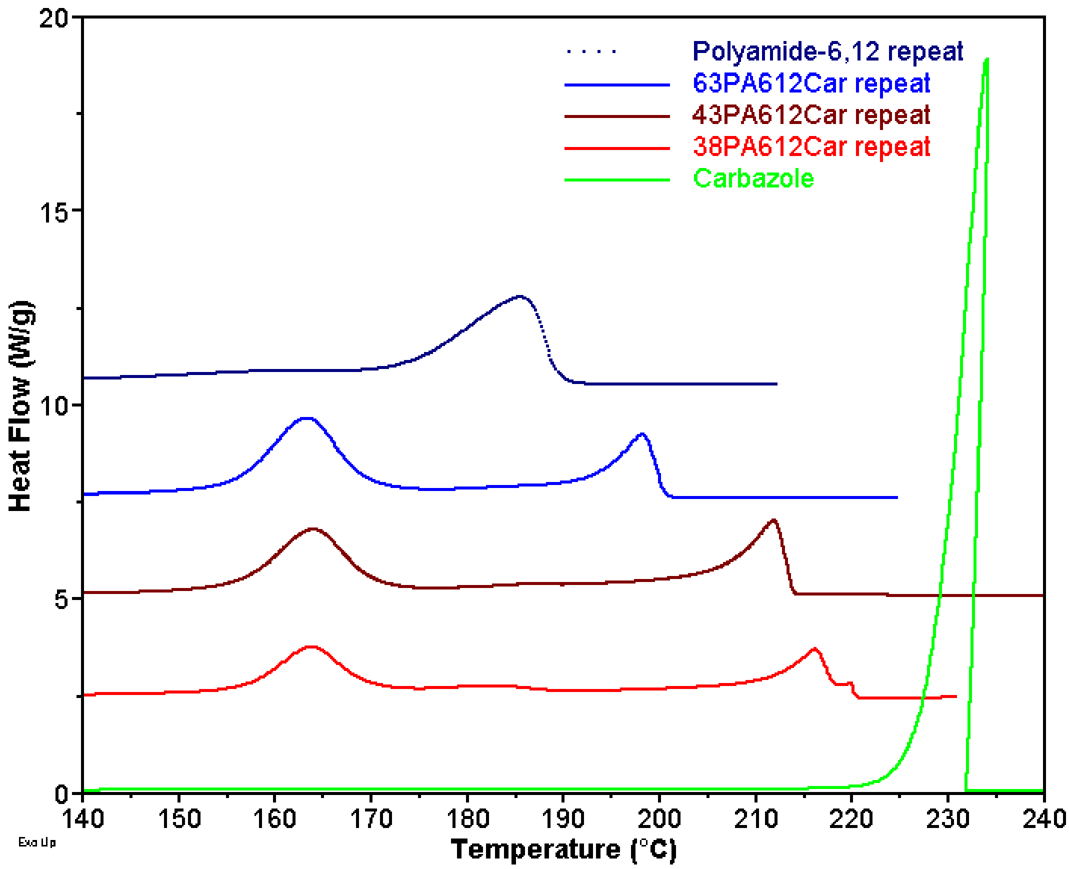

Figure 6-5 DSC thermograms of second crystallisation of pan blended polyamide-6,12/carbazole samples at 25 ^{0}C/min.

c) The 38PA612Car sample has approximately the same stages in crystallisation as previously, *viz.* a small spiky form crystallisation, a crystallisation slightly below that and a depressed polyamide crystallisation which is at the same temperature as with the 63PA612Car sample. The main difference is that the first peak has become smaller, less spiky and dropped from 228 ^{0}C to 220 ^{0}C. In addition, the peak at 217 ^{0}C has become slightly sharper. The move to lower temperatures for the spiky peak and reduction in size are due to the evaporation of carbazole noted for the thermogram of the second melting.

The picture for the second crystallisation is much the same as for the first crystallisation with eutectic formation, although modified by evaporation of carbazole for the sample with higher carbazole levels. The evidence for polyamide-6,12 with carbazole in the inter-lamellar space is repeated, but with a slightly sharper crystallisation peak.

6.3.2 Ampoule Material

6.3.2.1 Melting Temperatures (First melt in DSC) at 5 ^{0}C/min of ampoule material

The thermograms in Figure 6-6 show the melting profiles in the first DSC heating ramp for ampoule samples of polyamide-6,12, carbazole and their blends. They should approximate the second melting of the pan blended materials. There will be differences due to different prior cooling rates.

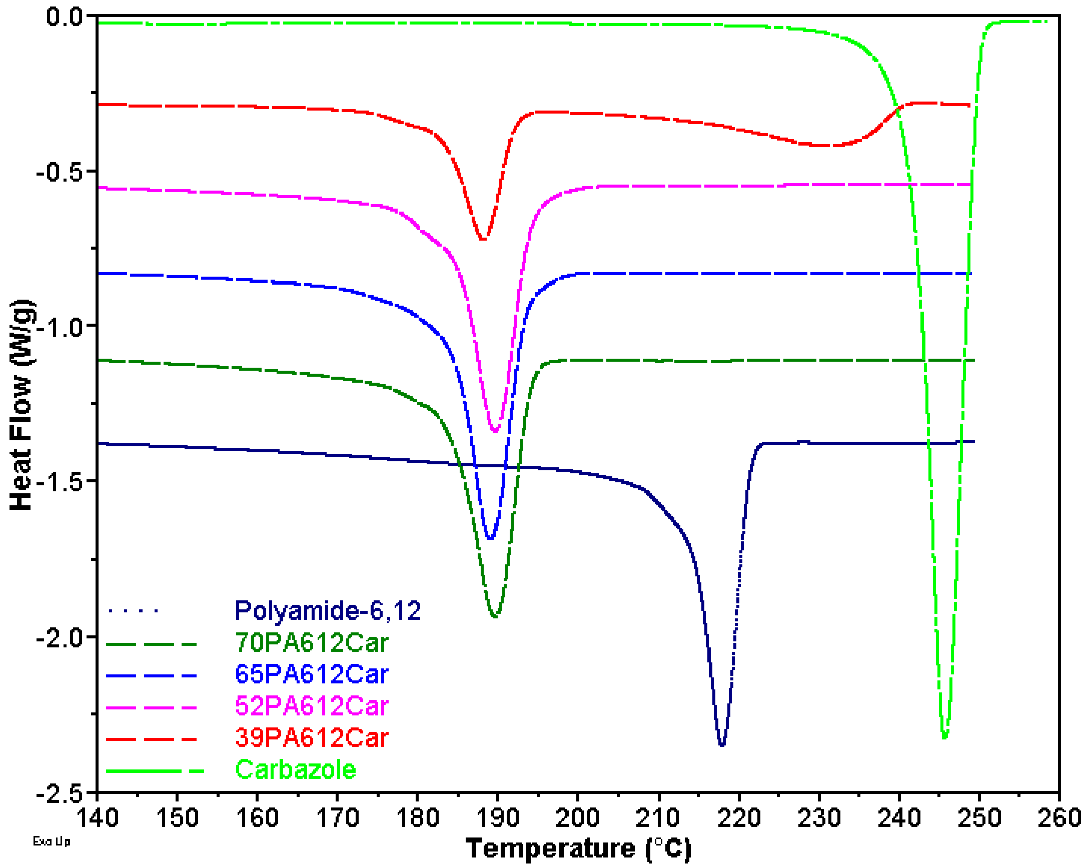

Figure 6-6 DSC thermograms of polyamide-6,12/carbazole ampoule samples first melting ramp at 5 ^{0}C/min in the DSC

a) The polyamide-6,12 sample has a main melting peak at 217 ^{0}C for the stable form with only a faint shoulder for the conversion of metastable lamellae to the stable form. The lack of a significant endotherm/exotherm pair prior to the main melting is due to the slow prior crystallisation in the ampoule.

b) 70PA612Car, 65PA612Car and 52PA612Car all have single melting peaks very nearly 30 ^{0}C below the polyamide-6,12 ampoule sample One aspect that distinguishes the three is the lead-in to the melting peak at 180 ^{0}C with there being a slight pre-melting for the 52PA612Car sample and even less of an effect on the other two. The other is the more rounded higher temperature side of the main peaks for 65PA612Car and 52PA612Car. These two appear to have slight vestiges of TLS peaks. The only indication that it is for an excess of carbazole rather than polyamide is that the 70PA612Car has none, meaning that 70% polyamide is close to the eutectic concentration.

c) The 39PA612Car sample has a main melting peak at almost the same temperature as for the other three blends but preceded by a slightly stronger deviation in the lead-in to the main melting peak. All the samples are showing similar behaviour to the start of the polyamide-6,12 ampoule sample. The region above the main melting peak is the same TLS peak form as other polyamide/carbazole blend combinations at high carbazole levels where excess carbazole is only dissolved up in the saturated solution at high temperatures.

These samples from ampoules show that the high temperature solution of carbazole in polyamide-6,12 is saturated near 70% polyamide at the depressed eutectic melting temperature near 190 ^{0}C. This provides confirmation of the results of the pan blended samples that this combination of materials differs noticeably from that of polyamide-6,9/carbazole blends in particular. In all cases we have seen single main melting peaks with the polyamide-6,12 materials from ampoules where the slower cooling has resulted in a different form from the fast cooled samples made in pans.

6.3.2.2 Overall Crystallinity

The percentages of polyamide were used with the total enthalpy of the first melting heating ramp to calculate the overall crystallinity of ampoule samples in the same manner as in Chapters 3 and 4. The results are plotted below in Figure 6-7.

It can be seen that, on average, there is an overall decrease in crystallinity with decreasing carbazole in the samples. The few results show a consistent decrease, the same as with polyamide-6/ and polyamide-6,9/carbazole but unlike the situation with polyamide-4,6/carbazole where results were more scattered. The lack of a linear relationship in crystallinity with concentration of polymer shows that the crystallinity is being depressed by the blending showing a non-zero free energy of mixing.

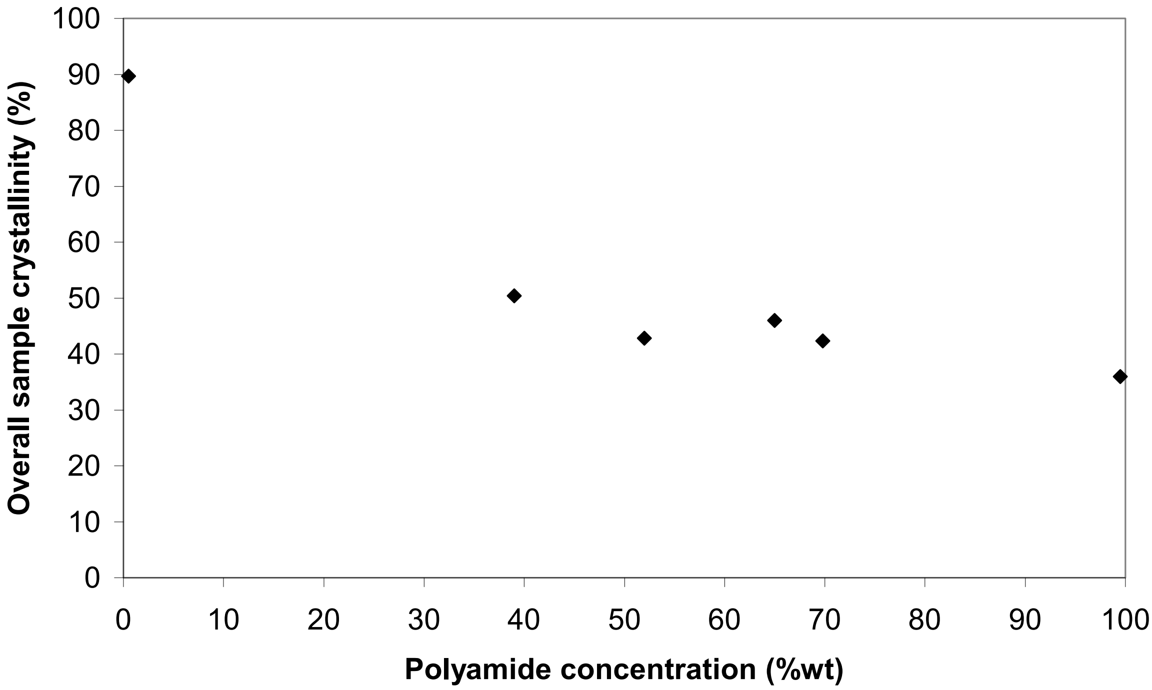

Figure 6-7 Overall crystallinity against weight percentage polyamide determined from TGA and total first DSC melting enthalpy of ampoule samples for polyamide-6,12/carbazole.

6.3.2.3 DSC Crystallisation Temperatures at 2 ^{0}C/min for remelted ampoule material.

Figure 6-8 shows the thermograms of the crystallisation of material melt-blended in ampoules, taken to the melt in DSC and then crystallised at 2 ^{0}C/min.

a) The 70PA612Car sample has a single crystallisation peak depressed by 25 ^{0}C below the normal polyamide-6,12 crystallisation peak. That peak does appear to have a slight, almost-vertical, section just before the top of the peak as the temperature is lowered. The peak rises after a slow beginning to the crystallisation. That implies the polyamide is slightly in excess under those conditions. The solution is almost 65 ^{0}C below the carbazole crystallisation temperature at that stage. Until that point, the third of the sample that is carbazole is being hindered from crystallising in the normal way by the presence of the polyamide. The polyamide would normally be increasing in viscosity due to the lower temperature but the solvent (carbazole) is lowering the viscosity. At that point, the supercooling of both materials that is the driving force for crystallisation has taken over, initiating the beginning of the polyamide crystallisation. That has altered the balance and the carbazole has then begun to rapidly crystallise. This again has altered the balance in this thermodynamically unstable solution and the rest of the crystallisable polyamide has crystallised. That curve can be seen in expanded form in Appendix A.

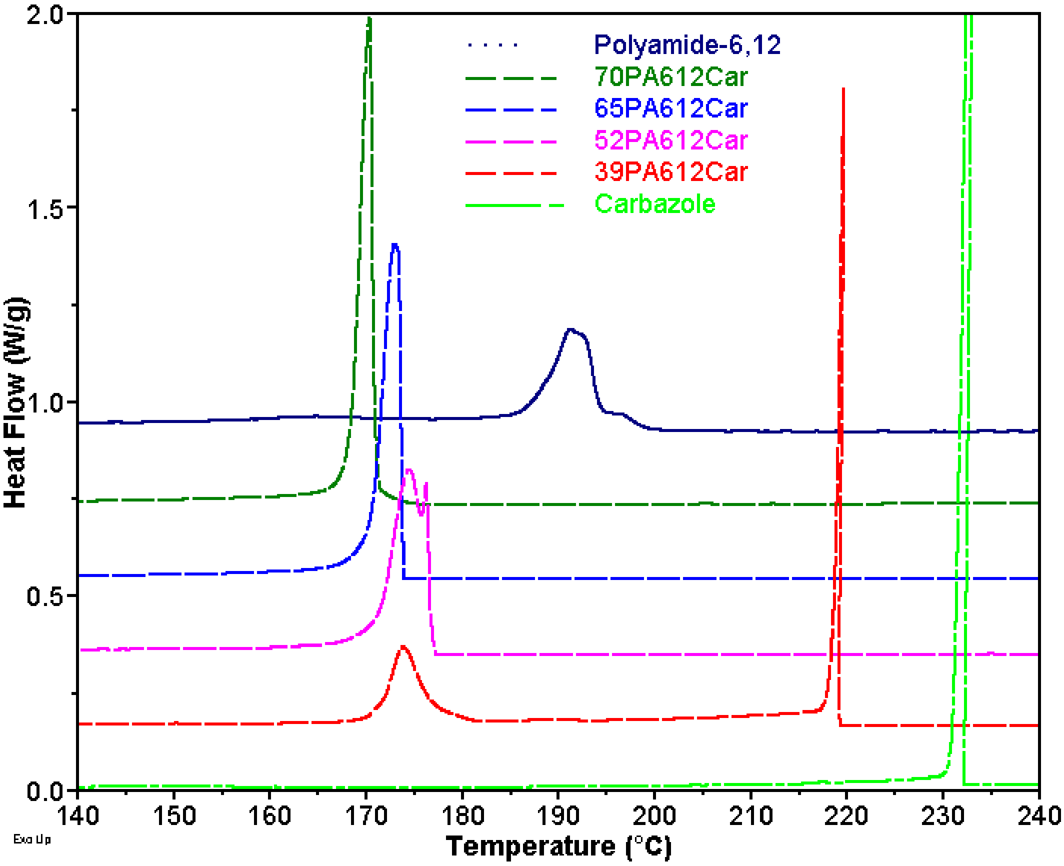

Figure 6-8 DSC thermograms of the first crystallisation at 2 ^{0}C/min in the DSC of polyamide-6,12/carbazole ampoule material.

b) The 65PA612Car has a near-vertical section for the single crystallisation peak, implying that the carbazole is driving the crystallisation (at almost exactly 60 ^{0}C below the normal carbazole crystallisation temperature). This is almost reaching the stage of 75PA6Car in Chapter 4 where there was a more pronounced break between the end of the carbazole crystallising and the rest of the peak. It is, however, at a noticeably lower polyamide level in the blend.

c) The 52PA612Car thermogram with a double peak 55 ^{0}C below the carbazole crystallisation temperature is showing more separation of the peaks with the carbazole being seen to start crystallising first and being overtaken by polyamide-6,12/carbazole crystallising at slightly lower temperatures after the tip of the spike.

d) The 39PA612Car is at such a high carbazole level that it can only sustain the whole sample in liquid form until 25 ^{0}C below the normal carbazole crystallisation temperature. At that point, a large amount of carbazole crystallises out quickly leaving a saturated solution at that temperature. The depressed polyamide-6,12/carbazole solution finally crystallises at exactly the same temperature as in the samples above.

All samples show themselves as a consistent series in their behaviour. We lave a single peak at 70% polyamide-6,12. We see the carbazole unable to remain stably in solution at such depressed temperatures, triggering earlier and earlier crystallisation of carbazole domains within the sample as the level of carbazole increases from sample to sample. There is a tendency to crystallise the carbazole earlier as the level of carbazole increases until by 39PA612Car the crystallisation of the two phases is separated by 40 ^{0}C. The similar forms of melting thermograms over a wide concentration range for the first three belie the subtleties more visible here. The lowest crystallisation (double) peak is for the sample with 70% polyamide but the first material to start crystallising is polyamide. In the 65% sample with polyamide it is the carbazole that begins to crystallise. It is clear that the optimal concentration is in this narrow range.

6.3.2.4 Crystallinity from first crystallisation in the DSC

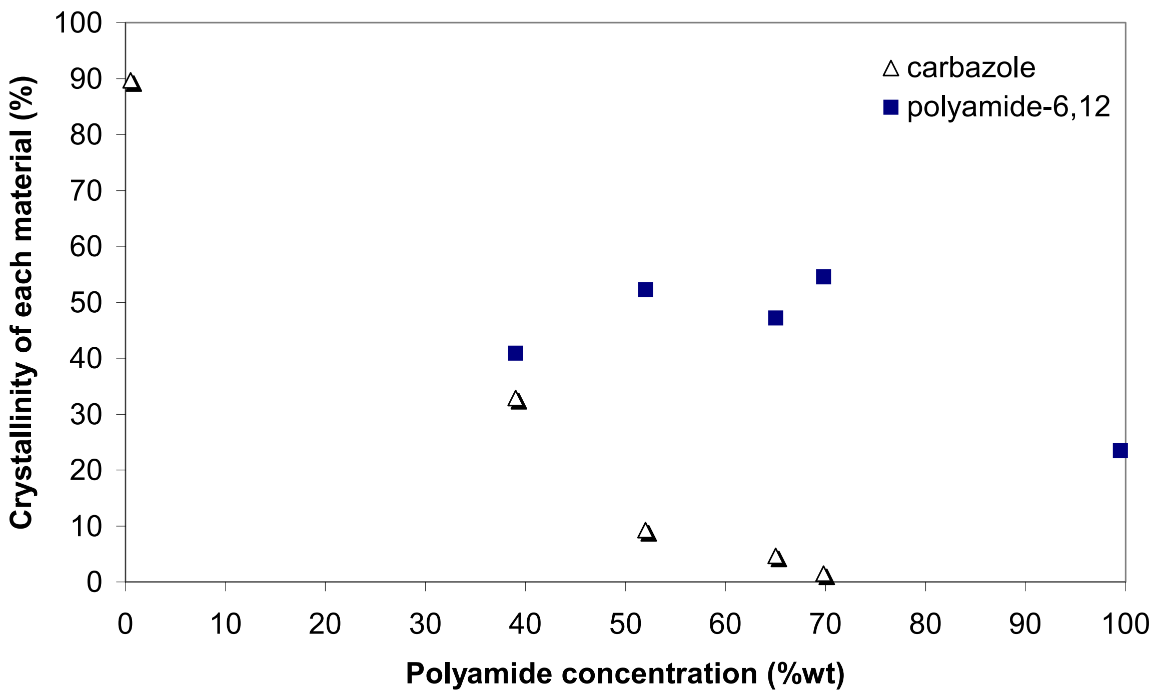

Figure 6-9 Crystallinity of carbazole and non-carbazole parts versus percentage polyamide, obtained from polyamide-6,12/carbazole crystallisation from the melt in the DSC.

Figure 6-9 below plots the crystallinity of the phase domains that are virtually pure carbazole in the first crystallisation cooling in the DSC. The crystallising peaks that are polyamide-rich domains are also plotted in the figure. It is quite clear from Figure 6-9 that the crystallinity of the carbazole falls off in an almost linear fashion with increasing polyamide content, reaching zero near 75% polyamide. That is in the region where the lowest crystallisation peak was seen and where the melting samples had a eutectic concentration. The carbazole in these samples with high polyamide levels is being incorporated closely in the solid without having the ability to crystallise separately. This would be with individual carbazole molecules between polyamide-6,12 chains in the general amorphous regions or in the amorphous interlamellar space.

The polyamides being studied here are semicrystalline which gives further complexity to the polymer/diluent situation because the diluent can solidify in the amorphous phase, causing depression of the glass transition temperature, or lie in the interlamellar space.

We see in the figure below that the crystallinity of the diluent is reducing in a nearly linear fashion to zero at just the concentration identified above where both materials crystallise at the same time. That is a similar situation to the one found by van der Heijden in his work, although he was dealing with a diluent/amorphous polymer system rather than a semicrystalline one.

The crystallinity of the non-carbazole phase is very much higher than that of pure polyamide from the ampoule. The results are similar to those of polyamide-6/ and polyamide-6,9/carbazole blends in earlier chapters.

6.3.2.5 Phase Diagram from first heating and cooling ampoule material in DSC

Figure 6-10 shows similar non-equilibrium eutectic phase diagrams to those of Chapters 4 and 5. Here again the crystallisation temperature of the diluent is higher than that of the polyamide. The depressed melting and crystallisation peaks for 52PA612Car should actually be to the right of their positions in the figure as there was significant evaporation of the diluent during the DSC runs.

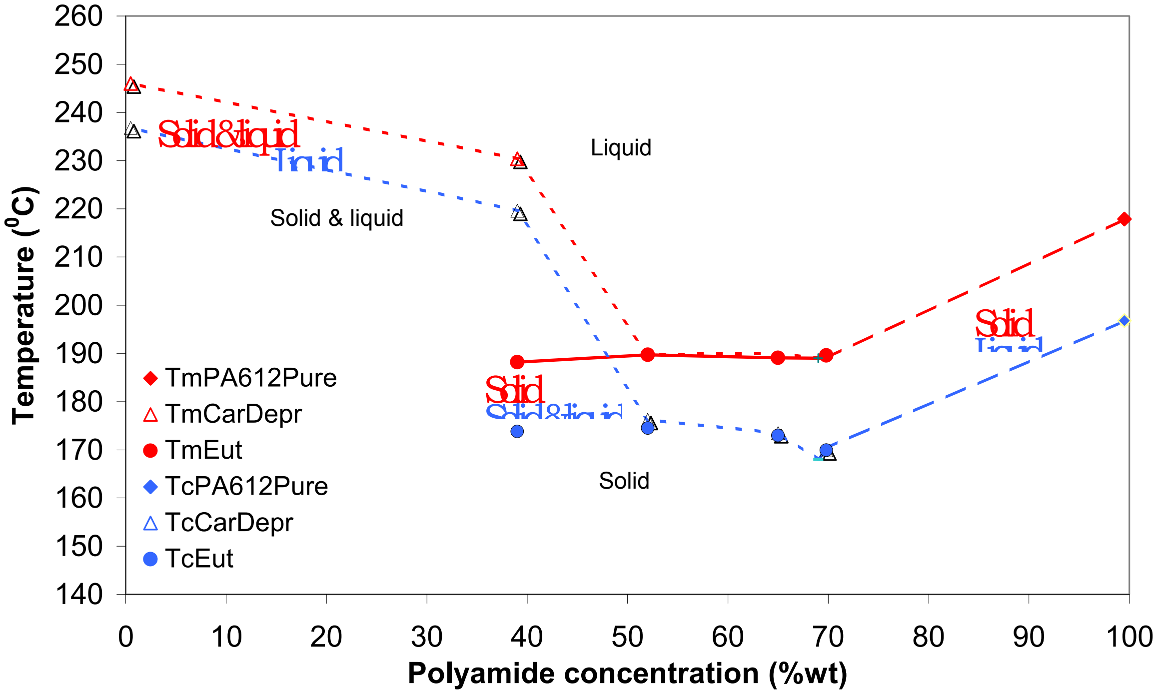

Figure 6-10 Non-equilibrium phase diagrams for polyamide-6,12, carbazole and their blends showing eutectic behaviour during heating and cooling.

6.3.2.6 Third Melting of materials/Second DSC Melt

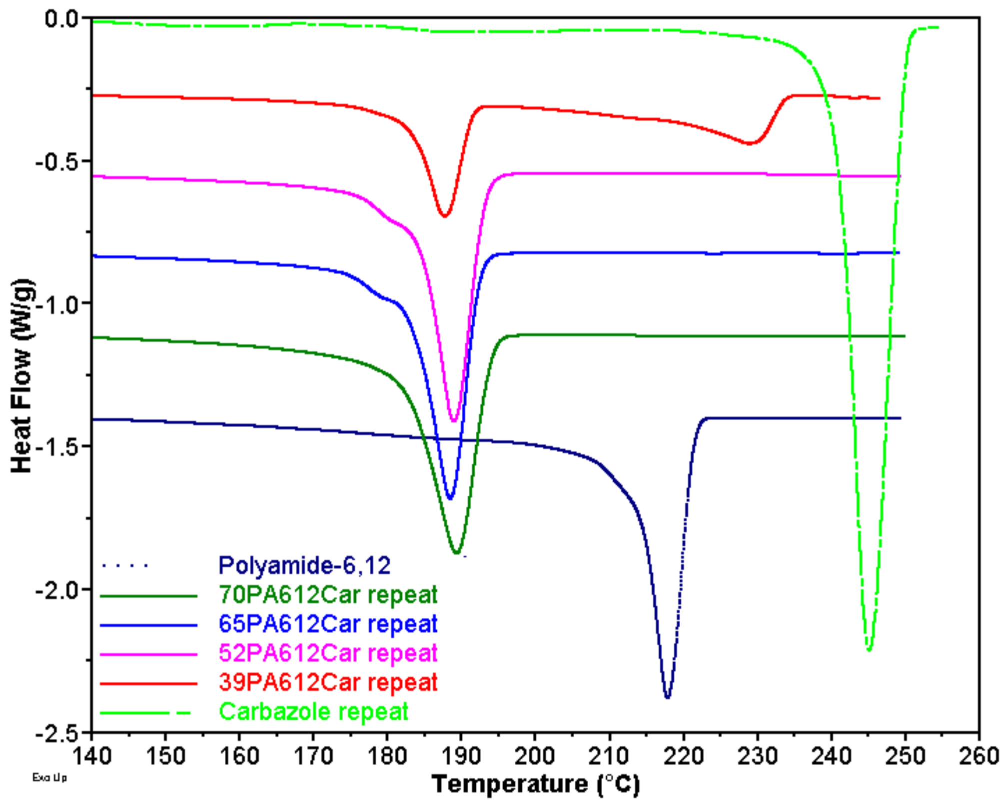

Figure 6-11 DSC thermograms of the second melt at 5 ^{0}C/min in the DSC of polyamide-6,12/carbazole ampoule material.

The ampoule samples in pans from the first DSC runs were passed through a repeat melt/crystallisation cycle in the DSC similar to chapters 3 to 5.

Figure 6-11 below shows the DSC thermograms of the melt portions of the repeat DSC runs.

There is virtually no difference between the first and second melts in the DSC of these polyamide-6,12/ccarbazole samples apart from peak temperatures differing by 1 – 2 ⁰C and the second (TLS) peak for excess carbazole dissolution with 39PA612Car being shortened due to carbazole evaporation.

6.3.2.7 Third Crystallisation of Materials/Second DSC Crystallisation at 2 ⁰C/min.

There are only small differences in Figure 6-12, compared with the first crystallisation in the DSC of these ampoule samples.

a) There is no significant change with the 70PA612Car sample.

b) The peak for 65PA612Car has dropped by 2 ⁰C due to loss of carbazole. There are hints of insignificant thermal activity at 212 ⁰C and 188 ⁰C.

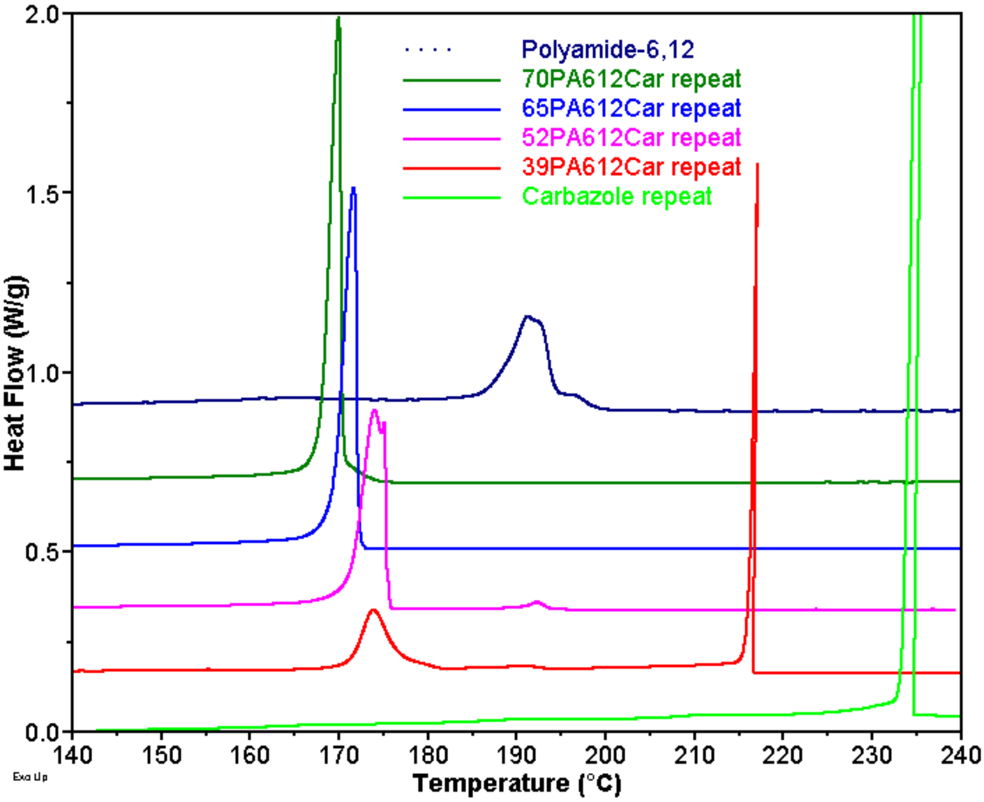

Figure 6-12 DSC thermograms of the second crystallisation in a DSC at 2 ⁰C/min of polyamide-6,12/carbazole ampoule material.

52PA612Car has carbazole-rich crystallisation taking place 2 ⁰C lower and the peak for the remainder is 1 ⁰C lower, both due to carbazole evaporation. There is a small disturbance in the thermogram near 192 ^{0}C because of slight crystallisation of near pure polyamide-6,12.

c) The spiky carbazole crystallisation has dropped by 4 ^{0}C for 39PA612Car but the second peak is unchanged, again consistent in the series with the loss of carbazole. There is a smaller polyamide-6,12 crystallisation at 190 ^{0}C than with 52PA612Car.

The small differences seen are associated with the evaporative loss of some carbazole during the extended period at elevated temperatures for the slow DSC cooling rate. There is a very small amount of polyamide-6,12 crystallisation at the polyamide-6,12 crystallisation temperature due to phase separation for the two highest level carbazole samples.

6.4 Fourier Transform Infrared Spectroscopy

No hydrogen bond interactions were found between polyamide-6,12 and carbazole in polyamide-6,12/carbazole blend samples using Photoacoustic FTIR measurements in the Mid Infrared and DRIFT FTIR in the Near Infrared. This result is the same as found in earlier chapters on other polyamide/carbazole blends. Detailed spectra are provided in Appendix D on CD.

6.5 Summary

This polyamide is different from the other polyamides previously studied in that it is an even-even polyamide with long carbon chains between the amide groups. These points affect the way in which the polyamide can crystallise. They are affecting the opportunities for polyamide-6,12 and carbazole to coexist in liquid form at high temperature and for the polyamide-6,12 to dissolve the carbazole as the blends are heated.

It was found in the pan blending that there was much less excess carbazole to dissolve at the higher carbazole level powder combinations and that the dissolution of excess only occurred at the highest level of carbazole. The carbazole is able to dissolve in melting polyamide-6,12 to a higher degree before the solution becomes saturated. That experience was also evident with the ampoule samples even though the slower prior cooling of the ampoule samples resulted in the polyamide-6,12 starting to dissolve from a stable rather than a metastable form.

The melting of powder mixes in pans at high levels of carbazole results in virtually all the carbazole being dissolved before the high temperature solution becomes saturated.

The crystallisation of pan blended samples having high levels of carbazole leads to much less carbazole crystallising out in the initial crystallising stages. The carbazole that is in the high temperature solution is more easily able to remain in solution with fast cooling rates.

Both of these are telling us that the solubility of carbazole in high temperature polyamide-6,12/carbazole solutions is noticeably higher on remelting than seen with the polyamide-6/ and polyamide-6,9/carbazole high temperature solutions from samples cooled at fast rates.

The ampoule samples, originally cooled at 2 ^{0}C/min, have showed similar increased solubility of carbazole in the blend upon remelting in the DSC.

We find differing crystallisation behaviour at the slower cooling rates compared to that of the other polyamides blended with carbazole in ampoules. The sample is far more inclined to remain completely as a liquid until much lower temperature, even at relatively high carbazole concentrations near 50%. The solutions are able to drop up to 65 ^{0}C below the normal carbazole crystallisation temperature before there is any crystallisation at all. This is approximately 25 ^{0}C below the normal polyamide-6,12 crystallisation temperature at those cooling rates.

The crystallinity of the carbazole drops linearly to zero with increasing polyamide content in this combination of materials, as for the other polyamides where the polyamide melting temperature is lower than that of the diluent. It does drop to zero here below 70% polyamide, lower than for the other two polyamides.

The non-carbazole crystallinity does show the same increase in crystallinity in the range 50-80% polyamide that was seen with other polyamides but the level of crystallinity has increased more than for the other polyamide/carbazole combinations.

The small differences between first DSC and second DSC melt/crystallisation cycles for ampoule samples are due to loss of carbazole.

This is similar to the observations for carbazole combined with other polyamides in ampoules.

A careful investigation with Mid Range and Near Infrared FTIR for interactions between polyamide-6,12 and carbazole in ampoule melt blended samples has delivered a similar result to the earlier investigations on polyamide-4,6, polyamide-6 or polyamide-6,9 blends with carbazole in that nothing could be found of any hydrogen bond interactions.

The main conclusions that can be drawn from this set of trials is that the compatibility between polyamide-6,12 and carbazole is better than that of the polyamide-6/ and polyamide-6,9/carbazole combinations. The behaviour of polyamide-6 in blends lies between that of polyamide-6,12/ and polyamide-6,9/carbazole blends. The latter two both have longer repeat units, showing that the even-even polyamide is much more compatible with carbazole than the even-odd polyamide.