

Chapter 7

POLYAMIDE-4,6 WITH PHENOTHIAZINE

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7.1 Introduction

We have looked at four polyamides combined with carbazole in the previous four chapters. The first polyamide, polyamide-4,6, had a melting temperature higher than the carbazole but the others had melting temperatures lower than the carbazole. In those chapters, we saw some quite large differences in the way the four polyamides melt blended with carbazole. We also saw behaviour that was common between the polyamides.

Chapters 7 to 10 will allow us to look at how the four polyamides behave when melt blended with phenothiazine. This is a small aromatic molecule, similar in shape to carbazole, but it includes a bulky sulphur atom on the opposite side of the structure to the N-H group. This material has a melting temperature of 186 °C compared with carbazole at 246 °C. All four

polyamides have melting temperatures above the temperature at which phenothiazine melts.

We will see differences due to the lower temperature at which phenothiazine melts despite polyamide-4,6 having a higher melting temperature than both of the blending materials. Phenothiazine and carbazole are slightly differently shaped molecules with differing electron density distributions.

The polyamide being investigated in this chapter, polyamide-4,6, is an even-even polyamide with the chain lengths of the $2N, 2*(N + 1)$ type. The diamine repeat sub-units are reasonably short and the diacid units are of medium length. These factors influence the way in which the polyamide can crystallise and give rise to the high polyamide-4,6 melting temperature just under $300\text{ }^{\circ}\text{C}$. This will be briefly alluded to in this chapter's summary. The repeat unit characteristics will become an important factor in the discussions of the General Conclusions chapter where all the results for the different polyamides and materials blended with them are brought together.

7.2 Thermogravimetric Analysis

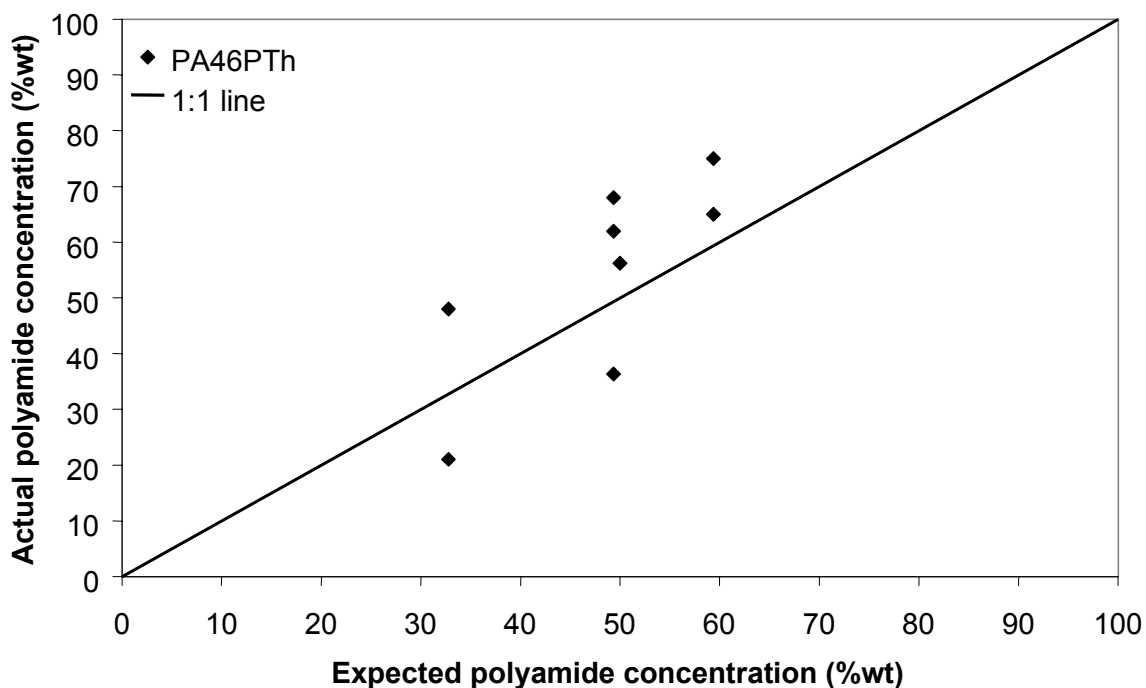


Figure 7-1 Actual versus expected weight percentage polyamide in polyamide-4,6/phenothiazine blend samples from ampoules as determined by TGA plateau levels at $300\text{ }^{\circ}\text{C}$ and compared with that expected from weights of materials used in the ampoules.

TGA was carried out on ampoule samples in order to determine the percentages of polyamide in the samples for crystallinity calculations. The

results are shown in Figure 7-1 in comparing the actual percentages of polyamide to those expected from the weights used in the ampoules.

Several of the points are much more than 5% away from the expected concentrations of polyamide. The large differences in polyamide concentration from the expected values in Figure 7-1, are real ones. These are variations due to imperfect mixing in the ampoules or to some molecular reorganisation during crystallisation in the ampoule. It is most likely that the variations are because a compromise was followed on the maximum temperature. On the one hand there was an aim to protect this polyamide from degradation leading to scission of some chains and also to further polymerisation resulting in increases in molecular weight of other chains at high temperatures. On the other hand the temperature had to be high enough that all polyamide lamellae were melted and the viscosity in the melt lowered sufficiently by elevated temperatures to ensure rapid diffusion of the two components of the liquid. The temperature used was either a little on the low side or phase separation took place resulting in less even distribution of the two components in various samples. We will see evidence in several parts of this chapter for phase separation taking place. Statistically there will be less predictable concentrations of polyamide in individual samples where phase separation has taken place, particularly if there has been substantial phase ripening.

7.3 Differential Scanning Calorimetry

Polyamide-4,6 normally has a single melting peak at close to 295 °C with crystallisation peaks in the range 259-275 °C, depending on crystallisation conditions, as was mentioned in Chapter 3. Phenothiazine melts close to 186 °C with crystallisation between 158 and 162 °C, depending on the cooling rate.

The high polyamide and low diluent melting temperatures did cause some problems in that the phenothiazine was being taken far above its melting temperature in order to reach the maximum working temperatures of the trials. Very minor deviations from perfection in sealing the hermetic DSC pans rapidly led to significant phenothiazine losses due to evaporation. These losses were confirmed by the practice of weighing pans after trials to check for phenothiazine loss. The combination of materials used for the

work in this chapter resulted in the biggest problems of evaporative loss encountered across all the work on the project and the problems for ampoule samples were the highest.

7.3.1 Pan Melt Blending

7.3.1.1 Melting Temperatures for first heating ramp of the dry powders at 5 °C/min

Individual thermograms for polyamide-4,6, phenothiazine and three blends shown in Figure 7-2 are described in detail below for heating powder mixes of polyamide-4,6 and phenothiazine to the melt at 5 °C/min in DSC pans.

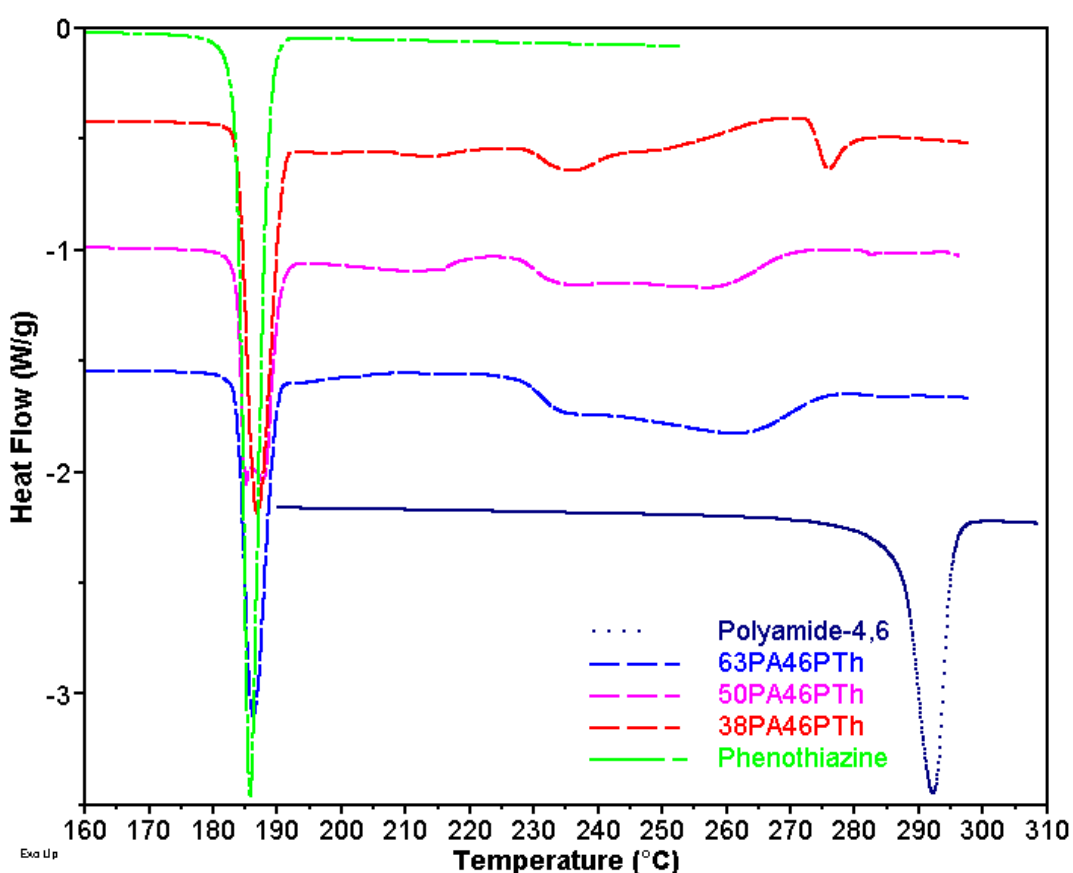


Figure 7-2 DSC thermograms during the first DSC melting at 5 °C/min of polyamide-4,6, phenothiazine powders and powder mixtures.

- a) The 63PA46PTh thermogram first has a phenothiazine melting peak at the temperature normally found for phenothiazine, but then displays a broad, flat peak over the range 230-280 °C with the polyamide-4,6 dissolving. The form of the thermogram is different from that encountered with polyamide/carbazole blends.

With those, we encountered dissolution of the higher melting material at temperatures lower than the normal melting temperature of the lower

material until saturation was reached. Further dissolution only accelerated with carbazole as the temperature increased. Eventually all of the excess higher melting material had been dissolved in a solution that was saturated at that temperature. Here, we have melting of the phenothiazine at exactly the normal temperature as if the polyamide was not there. It will be seen later in this chapter that polyamide-4,6 tends to phase separate at high phenothiazine concentrations having a very small solubility under those conditions. There is only slight evidence of crystalline polyamide dissolution in the 30 °C above the phenothiazine melting peak. The initial melting of phenothiazine is obviously at a high concentration of phenothiazine relative to the polyamide-4,6 concentration and it is occurring at temperatures well below the normal melting temperature of polyamide-4,6. It is not surprising that there is difficulty in dissolving the polyamide-4,6 powder into the phenothiazine-rich solution. The uneven, and slightly endothermic, thermogram height from 180-270 °C may point to some interaction between the molten phenothiazine and the amorphous part of the polyamide. At those temperatures the amorphous polyamide will be moving from being a rubbery material towards being a liquid. It is only at nearly 40 °C above the phenothiazine melting temperature that there is significant indication of the polyamide beginning to dissolve. There is some evidence of phenothiazine evaporation at high temperatures with a slight fall-off in the signal above 280 °C.

- b) 50PA46PTh is very similar except that there is a sharp double peak at the melting temperature of phenothiazine. The reason for the double peak is not clear. There is a slight depression of the thermogram, similar to the previous sample, just above the phenothiazine melting and before the polyamide melts/dissolves in the range 230-270 °C. These multiple weak exotherms are indicative of changing solubility of the various phases as the temperature is increased dissolving the polyamide powder for the first time. The temperature is being ramped at 5 °C/min and it is likely that there are also kinetic effects in the dissolution of polyamide powder in phenothiazine at temperatures below the normal polyamide melting temperature.

- c) The 38PA46PTh pan blended sample is similar except that some of the small amount of polyamide-4,6 is in the sample refuses to dissolve in the solution, undergoing a separate and sharp endotherm just under the normal polyamide-4,6 melting temperature. There is reduced solubility for polyamide-4,6 in the high temperature solution at high concentrations of molten phenothiazine. A similar situation existed for polyamide-4,6/carbazole blends with low levels of polyamide.

The picture emerging from this set of thermograms is of a phenothiazine melt at the normal phenothiazine melting temperature followed by a broad, flat double peak covering the temperature range 230-280 °C. It indicates limited solubility of polyamide in molten phenothiazine at high temperatures. The additional variant to this is for the sample with highest level of phenothiazine. There, the smaller percentage of polyamide was only partly soluble in phenothiazine, requiring virtually the normal melting temperature of polyamide-4,6 to melt the polyamide lamellae in the sample.

The thermograms display the reasonably indeterminate first melts/dissolutions of the higher melting materials as encountered in earlier chapters.

7.3.1.2 *Crystallisation for first cooling ramp of the molten blend at 25 °C/min.*

The thermograms in Figure 7-3 show the DSC results of cooling the high temperature solutions made from melting powder mixtures at 25 °C/min and also show those of the raw materials under the same conditions.

- a) 63PA46PTh, the sample with the lowest level of phenothiazine, has a single crystallisation peak at a temperature depressed by 12 °C from the normal polyamide-4,6 crystallisation temperature after a faint peak at the polyamide crystallisation temperature. There appears to be a small amount of phase separation resulting in some nearly pure polyamide-4,6 crystallising before the main crystallisation of polyamide-4,6 together with some phenothiazine. That main peak is the Flory-Huggins style behaviour with depression of polyamide-4,6 crystallising with some phenothiazine in the interlamellar space.
- b) 50PA46PTh, with more phenothiazine in the melt, has three crystallisation peaks, a peak for the crystallisation of phase separated, nearly pure polyamide-4,6 depressed by only 6 °C below the normal

polyamide-4,6 crystallisation temperature, an intermediate peak and the “spiky” peak for the crystallisation of excess phenothiazine slightly depressed from the normal phenothiazine crystallisation temperature. The intermediate peak is showing some formation of a polyamide-4,6/phenothiazine compound with polyamide-4,6 lamellae having some phenothiazine crystallising in the inter-lamellar space but the majority of the crystallisation is by either very polyamide-4,6-rich or phenothiazine-rich material. These peaks are showing both phase separation and the partial compatibility of the two materials at high temperatures. There is some polyamide-4,6 affecting the crystallisation of the phenothiazine because the crystallisation temperature is depressed further than with the pure phenothiazine and the 38PA46PTh samples.

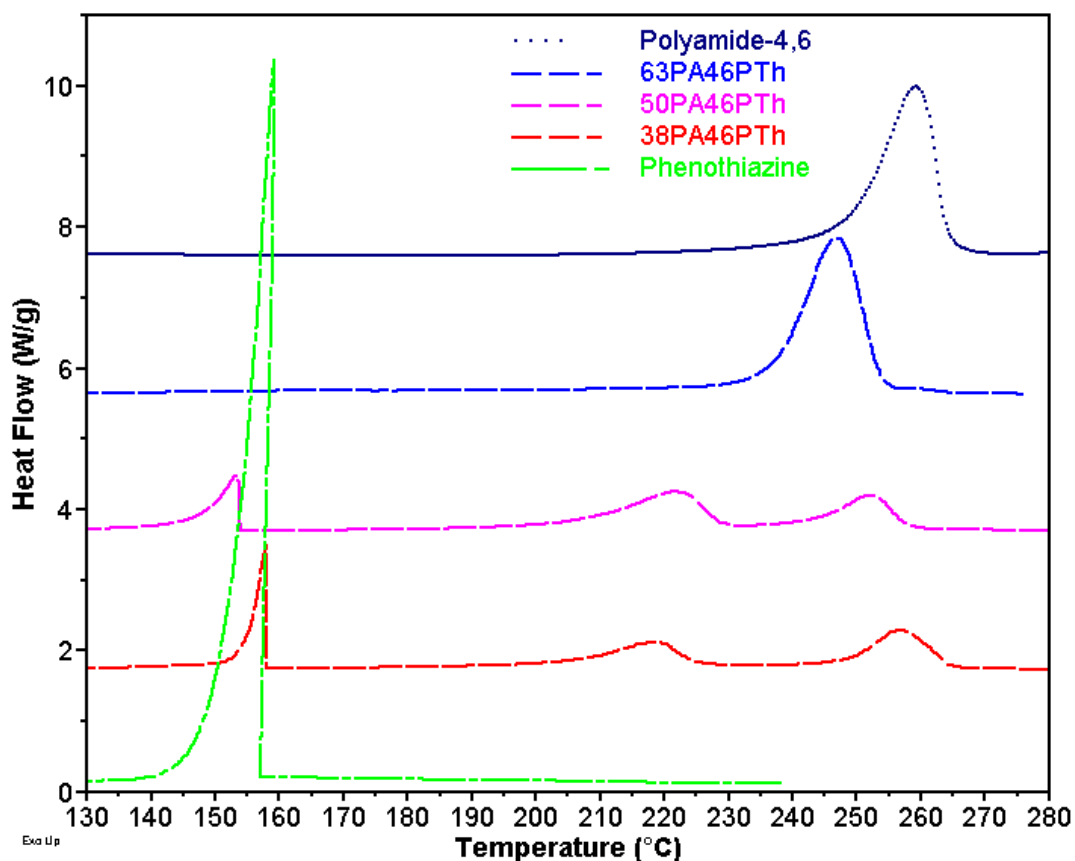


Figure 7-3 DSC thermograms for the first crystallisation of pan blended polyamide-4,6/phenothiazine, cooled from the melt at 25 °C/min.

- c) The thermogram for 38PA46PTh is similar to that of 50PA46PTh except that the crystallisation depressions of both polyamide-4,6 and phenothiazine are less than for the sample described above and the peak area of the middle peak is also reduced relative to the other two. The reduced depression of the polyamide-4,6 crystallisation is showing that

the solubility of polyamide-4,6 in the high temperature solution is reduced at high phenothiazine levels. This is a substantiation of the comments made on the first melting of the sample. The lack of depression for the phenothiazine crystallisation peak is showing crystallisation of the remaining phenothiazine is virtually pure phenothiazine. The change in the relative sizes of the three peaks is showing less compatibility between the materials at high phenothiazine levels. The small size of the phenothiazine peak near 160 °C is partly due to the evaporative loss of phenothiazine at the high temperatures required to melt the polyamide-4,6. The main reason is suppression of phenothiazine crystallinity.

These thermograms are supporting the notion of low solubility of polyamide-4,6 in phenothiazine at high temperatures, particularly when the level of phenothiazine in the solution is increased. They are also showing that at 50% phenothiazine and above it is possible to have polyamide-4,6 and phenothiazine crystallise at the same time. The small area in total under the peaks for those solutions with 50% phenothiazine and greater mean that much of the material becomes amorphous upon solidification under these conditions.

7.3.1.3 Melting Peak Temperatures for second heating ramp at 5 °C/min

The thermograms in Figure 7-4 are for the remelting at 5 °C/min of materials from the melt/crystallisation cycles described above.

- a) Sample 63PA46PTh differs substantially from that of the first melting. This whole set of samples had been taken to approximately 120 °C above the melting temperature of phenothiazine. In doing this, the 63PA46PTh sample had lost approximately 50% of the phenothiazine in the first melt/crystallisation cycle. That value has been determined from weighing the sample after the DSC run and assumes, based on experience, that the weight of the polyamide component of the sample is virtually unchanged. The sample could perhaps better be named 82PA46PTh or similar but the original naming has been kept for clarity in following individual samples through the repeat cycles. This sample has undergone two transformations between the two melt cycles. Firstly there has been the loss in phenothiazine just mentioned and secondly there has been a

better mixing of the two materials. A single, skewed peak can be seen that covers the melting of the crystalline polyamide-4,6/phenothiazine of the previous crystallisation integrated with the melting of polyamide-4,6. This differs strongly from the situation described in 7.3.1.1 where amounts of the powders had been put in the DSC pan with phenothiazine resting on top of the polyamide-4,6 grains and the resulting thermogram reflected the slow dissolution of those grains in the liquid.

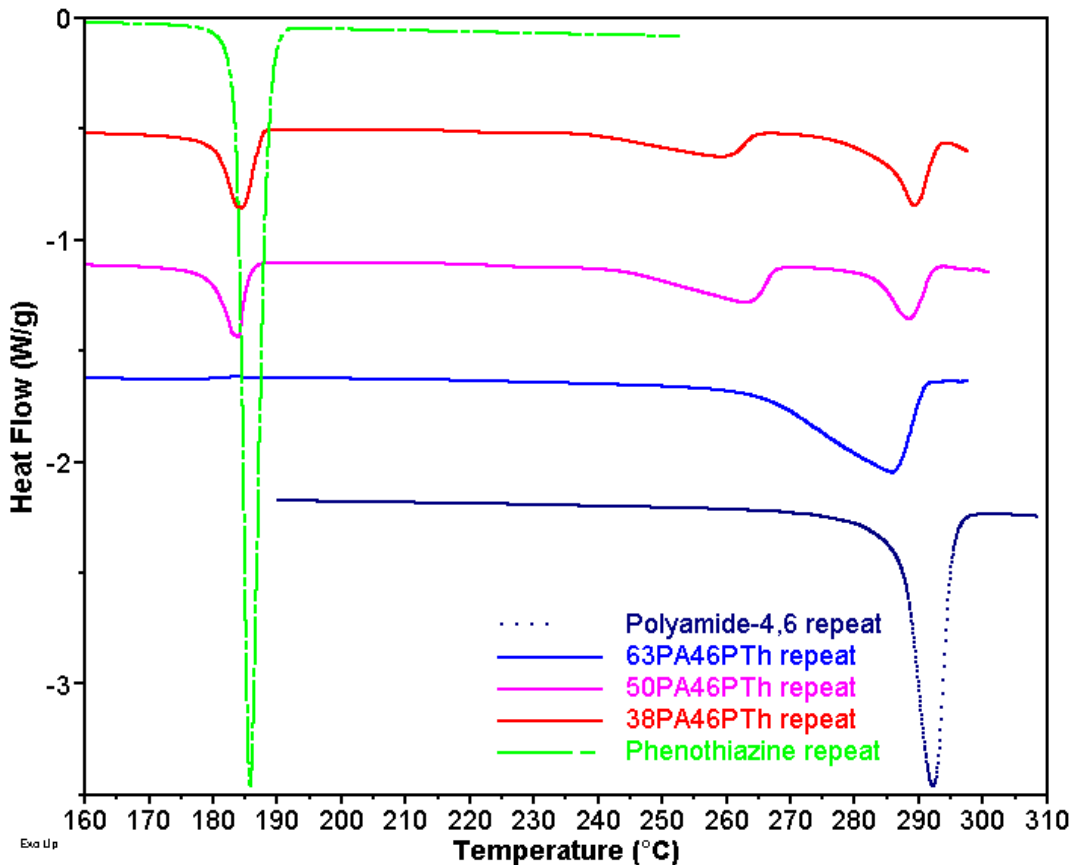


Figure 7-4 DSC thermogram at 5 °C/min of second melt of materials previously crystallised in DSC pans for polyamide-4,6/phenothiazine.

- b) The 50PA46PTh sample has lost 55% of the phenothiazine by taking the sample through the first heating/crystallisation cycle to 310 °C and back to room temperature. Alternatively, it could have been called 67PA46PTh for this DSC run. The three peaks in this thermogram are the melting of phenothiazine, the melting of polyamide-4,6/phenothiazine compound and the melting of residual polyamide-4,6. This corresponds closely with the reverse of the crystallisation process described earlier in section 7.3.1.2. That previous cooling of this sample had resulted in the crystallisation of polyamide-4,6, polyamide-4,6/phenothiazine and phenothiazine within the remaining amorphous material.

c) The 38PA46PTh sample had lost well over half of the phenothiazine by evaporation in the first heating/cooling cycle. The remaining phenothiazine was incorporated in the sample in very much the same manner as the (reduced) 50PA46PTh sample described above.

The repeat DSC runs of the three polyamide/phenothiazine samples here are dominated in their thermal responses by the prior loss of phenothiazine from the first heating/cooling cycle and the loss during this heating ramp. The sample with the highest polyamide content has changed to a (well mixed) slightly phenothiazine contaminated polyamide whilst the other two are providing confirmation, in reverse order, of the previous cooling results. Those showed the crystallisation of polyamide-4,6, then of a polyamide/phenothiazine compound and, lastly, crystallisation of phenothiazine. The three thermograms differed markedly from those for the melting/dissolution of the original powders in 7.3.1.1.

7.3.1.4 Crystallisation Peak Temperatures for second cooling ramp at 25 °C/min

Figure 7-5 shows the thermograms of the pan blended samples during their second cycle, cooling from the melt at 25 °C/min.

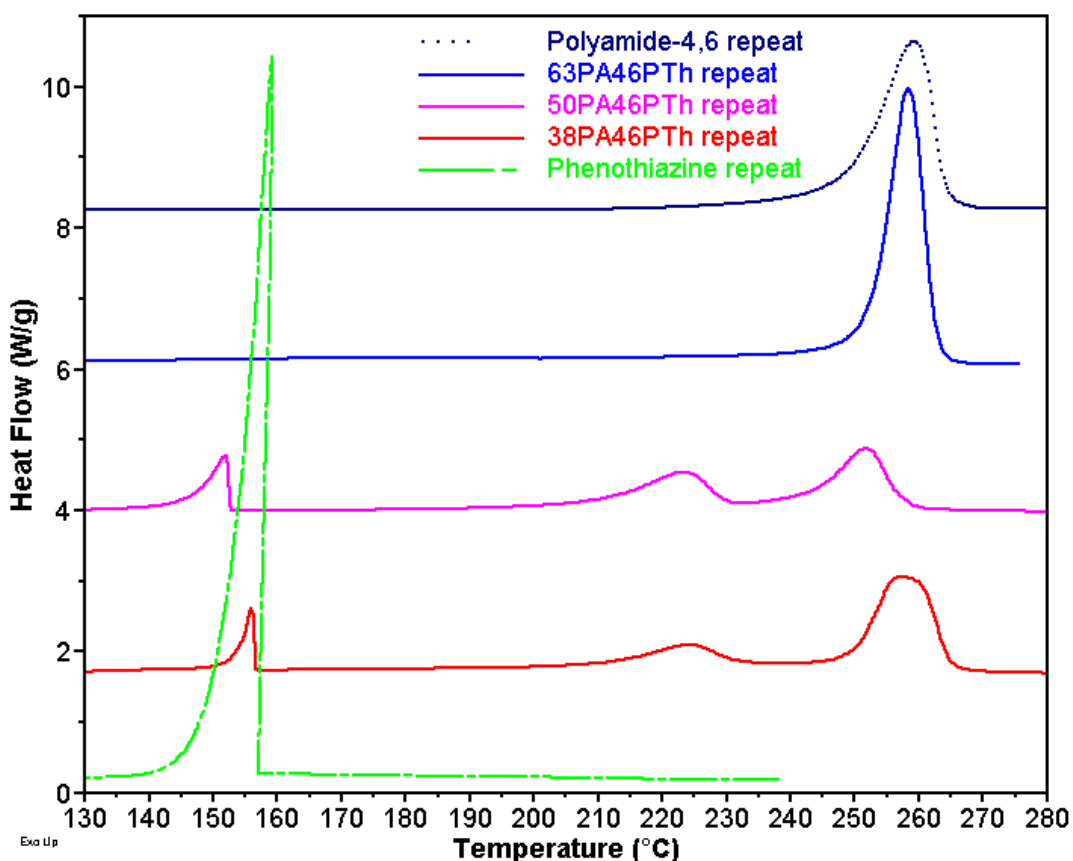


Figure 7-5 DSC thermograms of the second DSC crystallisation of pan blended polyamide-4,6/phenothiazine samples at 25 °C/min.

- a) The 63PA46PTh sample in re-crystallisation is showing the thermal response of further loss of phenothiazine, by now becoming virtually pure polyamide-4,6.
- b) The 50PA46PTh thermogram comprises the three peaks seen before for the crystallisation of polyamide-4,6, polyamide/phenothiazine compound and phenothiazine, very much at the previous temperatures observed.
- c) 38PA46PTh crystallises much as previously in the first DSC cycle except that the peak for polyamide-4,6 has increased at the expense of the peak for the polyamide/phenothiazine compound due to the loss of phenothiazine by evaporation.

The thermograms for the polyamide-4,6/phenothiazine samples have crystallised this time in the manner of the first crystallisation ramp except that curves have been modified because of the evaporative loss of phenothiazine.

7.3.2 Ampoule Material

It should be noted here that the ampoule sample 56PA46PTh was made at a time the ampoule heating ramps were still being refined. It is possible that the thermograms of the first melt in a DSC for this sample are not representative of the final process developed later. The effects of this should be zero after the first melt in the DSC.

7.3.2.1 Melting Temperatures (First melt in DSC) at 5 °C/min of ampoule material

The thermograms in Figure 7-6 show the melting profiles in the first DSC heating ramp for samples of polyamide-4,6, phenothiazine and their blends for materials previously crystallised in ampoules. They should be similar to those of the second melting of the pan-blended materials. There will be differences due to different prior cooling rates and the loss of phenothiazine in the first heating/cooling cycle for the pan blended samples. There had been no loss in the ampoule during crystallisation in the ampoule because it had been completely sealed during the process in the furnace.

This series of samples are probably best treated together rather than individually because they form a reasonably clear progression in their thermograms.

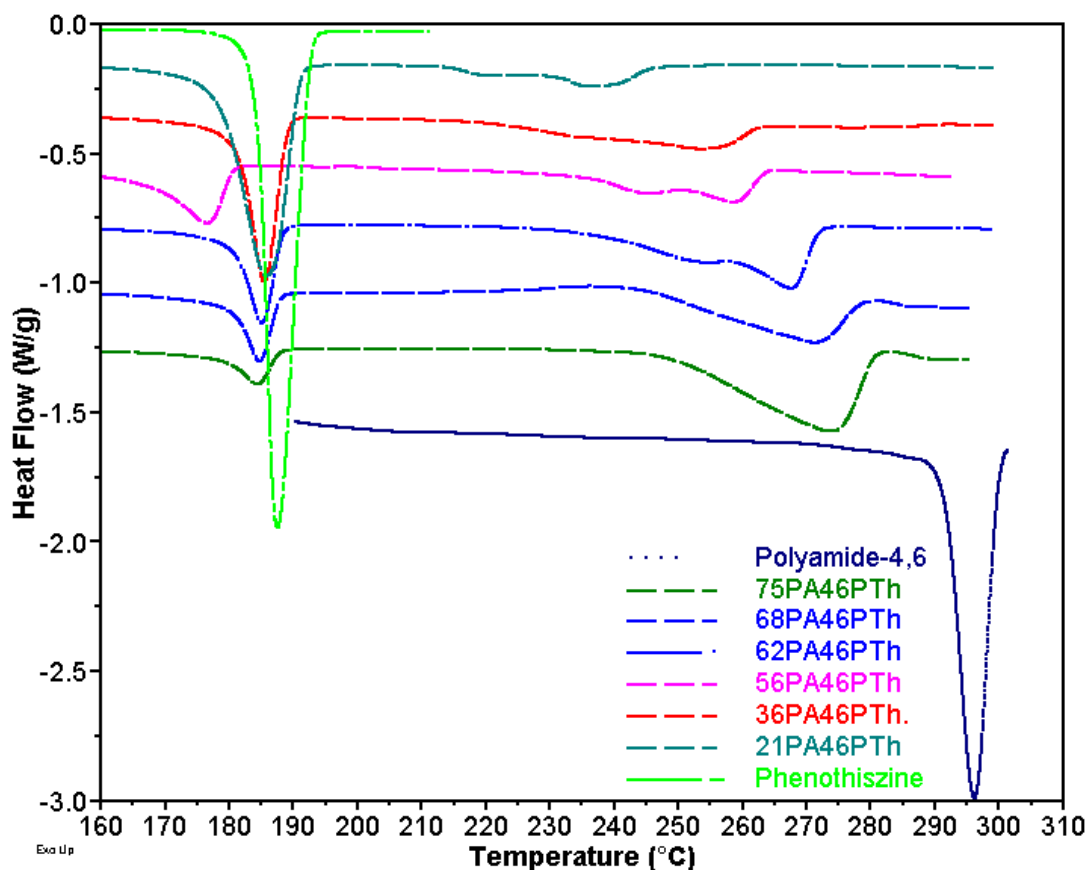


Figure 7-6 DSC thermograms of polyamide-4,6/phenothiazine ampoule samples first melting in the DSC at 5 °C/min.

All samples (except for 56PA46PTh) have initial melting peaks 2 – 3 °C below that of the ampoule sample of phenothiazine. That 56PA46PTh sample which was an exception had been, as previously mentioned, crystallised in an ampoule at the time when the cooling regime in the furnace was still being refined. Some of the past crystallisation history for that sample is playing itself out in this subsequent melting ramp. It has, nonetheless, been included here as part of the overall series made at differing polyamide concentrations.

There is a general trend for increasing size of the phenothiazine melting peak as a progression is made from the 75PA46PTh to the 21PA46PTh sample.

Single or double peaks are found above the phenothiazine peak and the temperature of the peak (or peaks) decreases with decreasing polyamide content. The double peaks may result from some phase separation during the cooling in the ampoule. The double peaks are occurring only for the higher phenothiazine concentration samples, where more phase separation has been found in past chapters. They have been seen earlier in this chapter and will be seen more in some of the future chapters. Double peaks had

been seen in Figure 7-4 for the second melting of the pan blended samples after fast cooling. These, however, had the upper peak consistently at the polyamide melting temperature with the lower peak dependent upon polyamide concentration. Phase separation is, thus, not a convincing explanation in this case. Another explanation of melting/re-crystallisation/melting of metastable crystallographic forms into more stable ones is also not entirely satisfactory as the temperature difference between the two peaks for a sample is over 15 °C. The difference between the metastable and stable peaks melting for rapid cooling of polyamide-4,6/carbazole in Chapter 3 was only 7 °C. The double peaks are to be seen again in Figure 7-11 for some of the thermograms from the second melting in the DSC. They are not related to any uneven cooling in the ampoules themselves. The reason for the double peaks in some of these samples therefore does not have a clear explanation.

The increasing size of the phenothiazine melting peaks is to be expected for an increasing amount of residual phenothiazine not being included in the polyamide-4,6/phenothiazine compound or, alternatively, incorporated to a small degree with the polyamide during the crystallisation in the ampoule.

The thermograms here can also be compared with those of the second melt of the pan blended samples in section 7.3.1.3. The major thermal difference in the creation of the ampoule samples is that they have previously been crystallised at 2 °C/min instead of 25 °C/min. The difference seen here at the melting stage is the absence of separate polyamide-4,6 melt peaks near 290 °C. The pan blended samples with high phenothiazine levels crystallised some of the polyamide-4,6 due to phase separation with the fast cooling. That did not happen with the ampoule samples because there was more time during the slower cooling ramp to crystallise the two materials together without having the polyamide-4,6 crystallise separately at an earlier stage.

7.3.2.2 Overall Crystallinity

The results of ampoule sample overall crystallinity calculations are plotted below in Figure 7-7 along with a curve for a linear relationship in crystallinity based on a molar volume percentage. The overall percentage of crystallinity in the samples has a broad minimum at approximately 60% polyamide with higher crystallinity for the pure phenothiazine and

polyamide-4,6. The minimum for the samples near 60% polyamide concentration is pointing to most of the sample mass being tied up in the amorphous phase as they crystallise in the ampoules. The two materials are adversely affecting the crystallinity of each other.

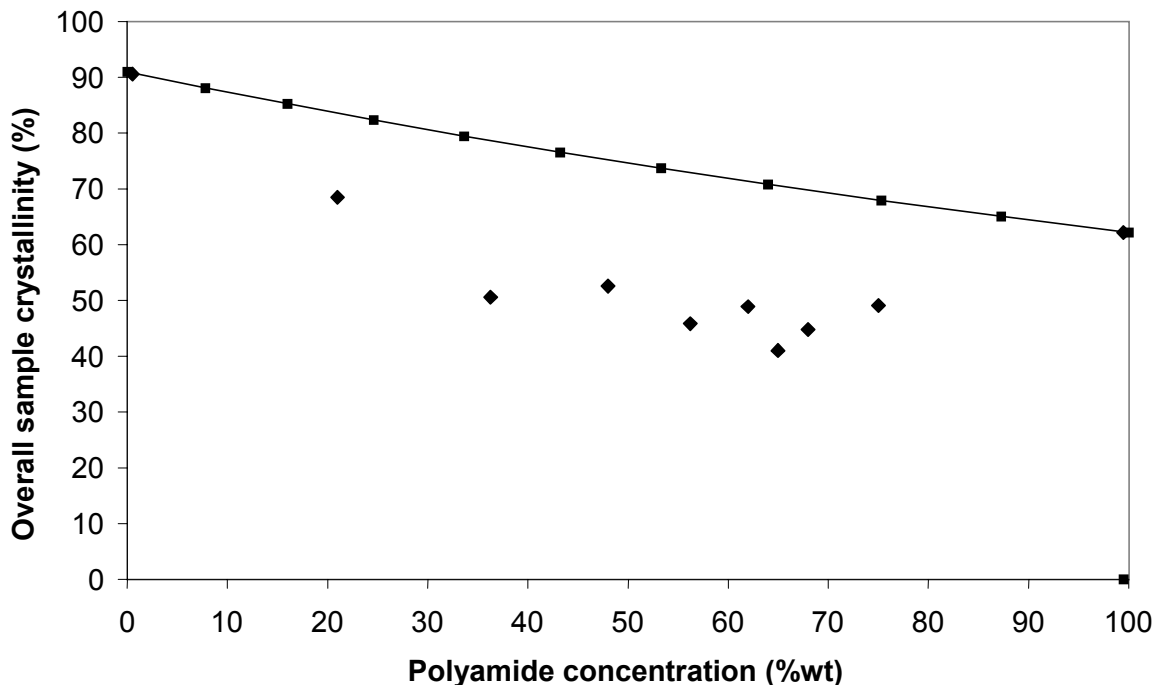


Figure 7-7 Overall crystallinity determined from TGA and total first DSC melting enthalpy of polyamide-4,6/phenothiazine samples from ampoules. This reflects the crystallinity at the time the samples are taken from ampoules.

A linear relationship for colligative properties is usually based on molar volumes. In this case the specific density of both crystalline and amorphous polyamide-4,6 lie between 1.0 and 1.1 and that of phenothiazine is 1.38. That means a dip of 6-8% in crystallinity between 42 and 43 wt% polyamide based on a linear relationship on a molar volume basis. The maximum dip found in crystallinity calculations with respect to that line is even 25% lower.

7.3.2.3 DSC Crystallisation Temperatures at 2 °C/min for remelted ampoule material.

Figure 7-8 shows the thermograms of the crystallisation of material melt-blended in ampoules, taken to the melt in the DSC and then crystallised at 2 °C/min cooling rate.

- a) The thermogram for 75PA46PTh shows the crystallisation of polyamide-4,6 depressed by 20 °C because of the presence of phenothiazine followed by the crystallisation of a very small amount of phenothiazine some 12 °C below the phenothiazine crystallisation

temperature. This is showing the ability of some of the two materials to crystallise at the same time in a Flory-Huggins style depression of the crystallisation temperatures.

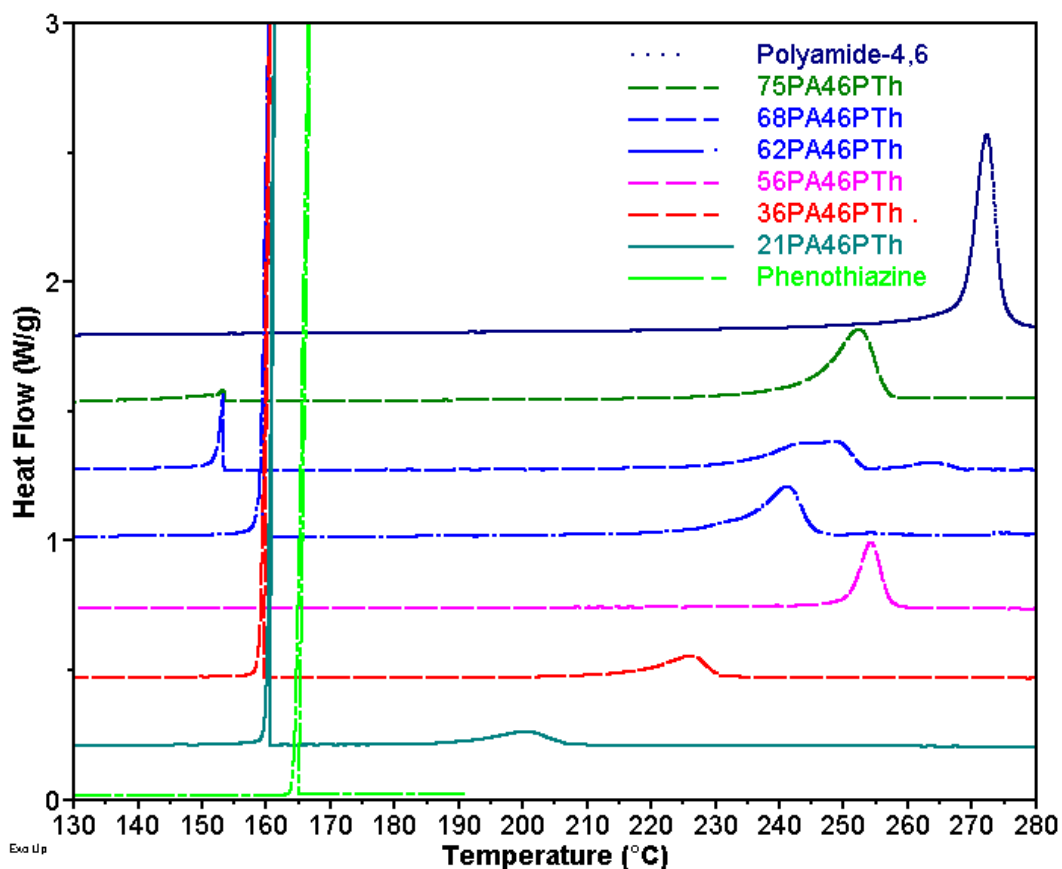


Figure 7-8 DSC thermograms of the first crystallisation at 2 °C/min in DSC of polyamide-4,6/phenothiazine ampoule material and the weight loss encountered over two melt/crystallisation cycles.

- b) The 68PA46PTh sample shows minor crystallisation of polyamide-4,6 depressed by about 8 °C followed by the crystallisation in two stages of polyamide-4,6/phenothiazine depressed in a double peak by a total of 25 °C. The double peak is most likely due to uneven consistency of the concentration in the sample. Finally there is the crystallisation of phenothiazine depressed by 12 °C.
- c) The 62PA46PTh thermogram shows only two peaks, a polyamide-4,6/phenothiazine peak depressed by 30 °C and a phenothiazine crystallisation peak depressed by 4 °C below that for phenothiazine. The reasoning here on the magnitude of depressions is the same as in the 75PA46PTh sample but with a greater phenothiazine concentration.

- d) The 56PA46PTh sample has a single peak depressed by 20 °C below the polyamide-4,6 crystallisation temperature. It is also a sample where there has been substantial loss of phenothiazine by evaporation, as indicated by post-DSC weighing. It has been mentioned earlier that having to take samples with phenothiazine to the very high melting temperature of polyamide-4,6 for the trials presented problems with ensuring that the hermetic pan seal was perfect. There was no way to easily determine how well the pan was sealed prior to the DSC run. The other alternative, that the different prior history of this sample to the rest may have been responsible does not have a strong case as the prior history will have been removed by the melting process. That sample had been taken 40 °C above the highest temperature of thermal transitions.
- e) 36PA46PTh is showing a peak 45 °C below the polyamide-4,6 crystallisation temperature and a phenothiazine peak depressed 3-4 °C below the phenothiazine crystallisation. The first peak is a very substantial drop in crystallisation temperature and indicates some concurrent solidification of phenothiazine with polyamide-4,6.
- f) The thermogram of 21PA46PTh has its first peak during crystallisation at more than 70 °C below the crystallisation temperature of polyamide-4,6. This is an extremely large depression of the crystallisation temperature and points towards a combined crystallisation of polyamide-4,6 and phenothiazine. The second crystallisation peak is only 2-3 °C below the crystallisation temperature of phenothiazine. That would be expected with the relatively low concentration of polyamide in the sample.

There is a definite pattern in the thermograms in Figure 7-8 of large depression of the first crystallisation peak proportional to the phenothiazine concentration in the sample. The reduction in crystallisation temperature by more than 70 °C for one sample shows that there can be a strong Flory-Huggins style interaction between the two materials. The depression of crystallisation temperatures for each materials appears to be linear in concentration of the “contaminant” once evaporative loss of phenothiazine has been accounted for. The two materials are able to solidify together, resulting in the extremely large crystallisation depression.

A comparison with the (comparable) second crystallisation of the pan blended samples shows that the first crystallisation peak, of polyamide-4,6, is missing before the crystallisation peak for polyamide/phenothiazine with samples having higher levels of phenothiazine. That single peak generally found here above the phenothiazine crystallisation occurs because the cooling sample has more time at the slower cooling rate here to crystallise with phenothiazine in the inter-lamellar space rather than polyamide-4,6 partly phase separating with rapid cooling.

The depression of the phenothiazine crystallisation temperature is far more modest and appears to be capped at a maximum depression of 12 °C when the polyamide concentration has risen to 63%.

The thermograms are strongly affected by the evaporative loss of phenothiazine from some samples, as evidenced by lesser crystallisation temperature depression. The loss of phenothiazine results in the sample being more concentrated in polyamide than the blend that was begun with.

7.3.2.4 Crystallinity from first crystallisation in the DSC

The crystallinity of phenothiazine and polyamide, as displayed in Figure 7-9 from the first cooling ramp in the DSC, does have some limitations because of the evaporative loss of phenothiazine to varying degrees from the samples.

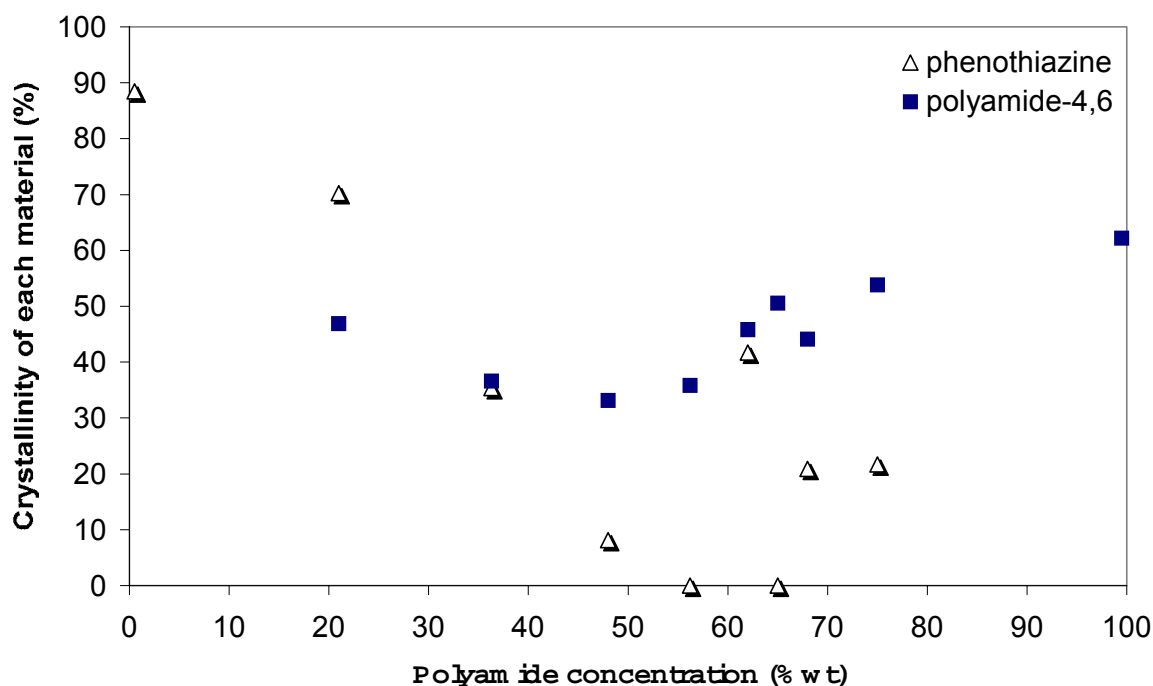


Figure 7-9 Crystallinity of phenothiazine and polyamide from the first crystallisation in the DSC at 2 °C/min of polyamide-4,6/phenothiazine blends made in ampoules.

There is a drop in the phenothiazine enthalpy of crystallinity as the polyamide level is increased. The values are, however, scattered as was found with the polyamide-4,6/carbazole combination in Chapter 3 and unlike the consistently more linear relationships found in Chapters 4 to 6. We will see evidence in the remaining chapters that they also have scatter in phenothiazine enthalpy of crystallisation. The polyamide crystallinity rapidly increases again from a substantial minimum as the polyamide concentration is reduced below 50%.

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

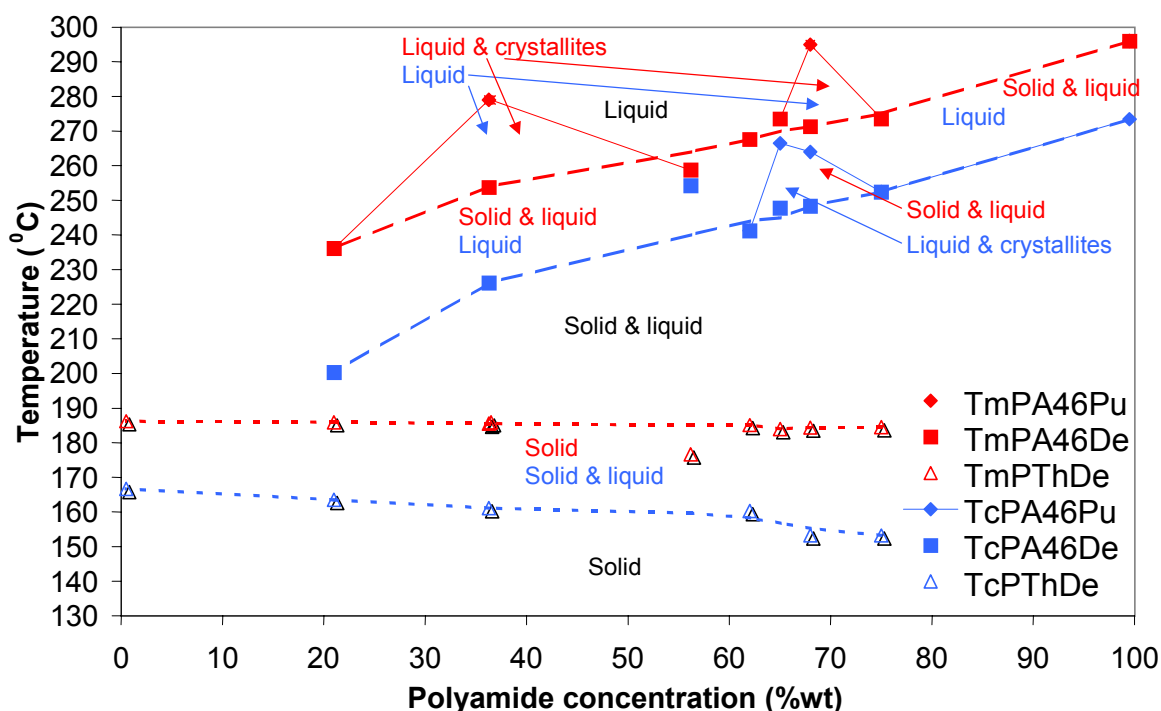


Figure 7-10 Non-equilibrium phase diagrams for polyamide-4,6, phenothiazine and their blends showing Flory-Huggins style depressions of melting and crystallisation temperatures.

The Flory-Huggins style depression of the melting/crystallisation of blends of polyamide-4,6 and phenothiazine with each material depressing the transition temperature of the other can be seen clearly in Figure 7-10 without the distraction of anomalies that usually occur near the crossover points. This is similar to the case of polyamide-4,6 with carbazole where the polyamide crystallisation temperature is higher than that of the diluent. In this case we can also see some melting/crystallisation of small regions of relatively pure polyamide-4,6.

7.3.2.6 Third Melting of materials/Second DSC Melt

The ampoule samples were passed through a repeat melt/crystallisation cycle in the DSC, as was done in earlier chapters.

Some evaporation of phenothiazine has taken place in between the first and second DSC runs of the ampoule samples. The effect will be greater than in the pan blended samples because of the protracted times spent at high temperatures caused by the slower cooling ramp here Figure 7-11 below shows the DSC thermograms of the melt portions of the repeat DSC runs on the ampoule samples.

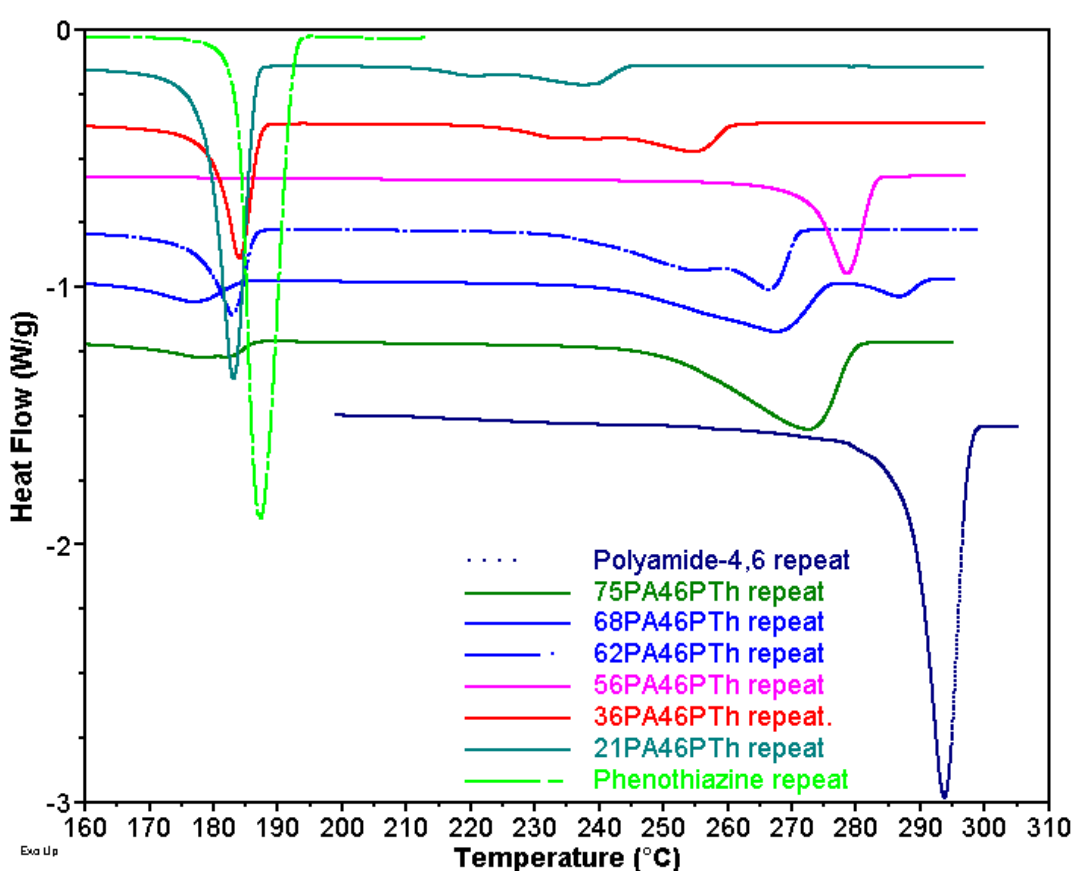


Figure 7-11 DSC thermograms of the second melt at 5 °C/min in the DSC of polyamide-4,6/phenothiazine ampoule material.

The pattern of the thermograms in Figure 7-11 for the repeat DSC melting is very similar to that of the first crystallisation in the DCS of samples made in ampoules. The exceptions are the 56PA46PTh sample that had already been noted to have had evaporative phenothiazine losses and the 68PA46PTh sample that shows some melting of nearly pure polyamide-4,6 as was seen in the previous crystallisation of the sample.

7.3.2.7 Third Crystallisation of Materials/Second DSC Crystallisation

The differences in Figure 7-12 compared with the first crystallisation in the DSC of these ampoule samples are not large if phenothiazine evaporative loss is taken into account.

There has been slightly more of a tendency to crystallise out some of the polyamide and phenothiazine separately. That occurred with polyamide-4,6 crystallisation for 36PA46Car and 68PA46PTh. The phenothiazine crystallised out separately to a greater extent with 68PA46PTh and the small phenothiazine crystallisation of 75PA46PTh had become broader and ill defined.

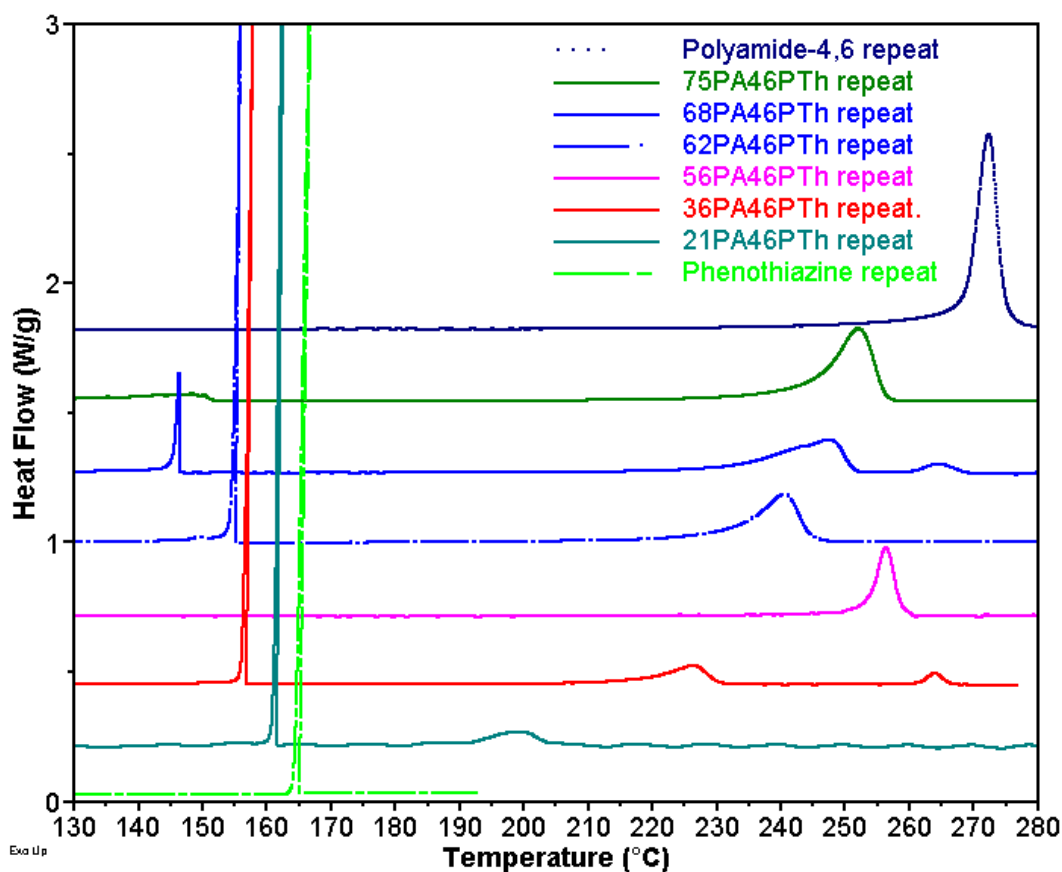


Figure 7-12 DSC thermograms of the second crystallisation at 2 °C/min in a DSC of polyamide-4,6/phenothiazine ampoule material.

The only other noteworthy change was the increase in phenothiazine crystallisation depression by 1 – 2 °C.

The thermogram for 21PA46PTh displays noticeable noise in what should be a straight line apart from the (real) peak near 200 °C and the phenothiazine crystallisation near 160 °C. There were occasional problems with noise that are continuing to be worked on with the instrument manufacturer.

7.4 Fourier Transform Infrared Spectroscopy

FTIR in the Mid-Range and Near Infrared was carried out on samples of polyamide-4,6/phenothiazine melt blended in ampoules. In neither region of the electromagnetic spectrum was there any evidence of effects due to hydrogen bond interactions between the materials. Spectra can be found in Appendix D on CD.

7.5 Summary

The combination polyamide-4,6 with phenothiazine had been expected to perform thermally in a similar manner to the polyamide-4,6/carbazole blends in Chapter 3. In both cases, the polyamide melts at higher temperatures than the material with which it is being blended and the two diluent molecules have reasonably similar molecular shapes. The phenothiazine has a melting temperature at 186 °C, much lower than the 246 °C carbazole melting temperature. That low melting temperature complicated the observations because working temperatures for the polyamide-4,6 had to be as high as 307 or 312 °C to melt this polyamide. That caused much more loss in phenothiazine because of evaporation. The low melting temperature of the phenothiazine also meant that the polyamide was much further thermodynamically from its normal melting temperature, making dissolution of polyamide-4,6 lamellae into the liquid more difficult. That point affected the initial dissolution kinetics of pure polyamide-4,6 grains in the powder blends. The initial melting of phenothiazine produced a highly phenothiazine concentrated solution that sits unfavourably for dissolution of polyamide-4,6.

The carbazole had dissolved as much polyamide as possible (up to nearly the same mass of polyamide-4,6) during the first heating of carbazole and polyamide-4,6 powders in Chapter 3. This was associated with a depression of the carbazole melting temperature by some 10-15 °C. Further polyamide could only be dissolved as the temperature was increased. The rate of dissolution increased with temperature until all polyamide had dissolved or the polyamide-4,6 melting temperature was reached, where any remaining polyamide would melt at the normal polyamide-4,6 temperature.

The change seen for this chapter with polyamide-4,6/phenothiazine blends is that there is no depression of the phenothiazine melting peak near 186 °C.

There is also little thermal activity to be seen until approximately 230 °C where there is a broad flat melting/dissolution of the polyamide. This has a reasonably sharp onset and finishing near 270 °C, depending upon the proportion of polyamide in the sample. Not all the polyamide could be dissolved at low levels of polyamide in the mix. The temperature needed to be increased to just under the polyamide-4,6 melting temperature in order to melt all the polyamide. It therefore appears very difficult to dissolve polyamide-4,6 in phenothiazine until 230 °C is reached or, alternatively, the kinetics of the dissolution are slow. That situation was quite different with material already melted once, and where the two materials were more intimately mixed at a molecular level.

Crystallisation of the high temperature solution is dependent upon both concentration and cooling rate. There was generally a depression of crystallisation, regardless of cooling rate and there was no separate phenothiazine crystallisation at concentrations significantly over 60% polyamide. The depression appears to be proportional to the amount of phenothiazine, based on some measurements of sample mass after cooling to room temperature.

Crystallisation at high cooling rates (25 °C/min) with lower percentages of polyamide resulted in crystallisation of some of the polyamide-4,6 at temperatures close to the normal polyamide-4,6 crystallisation temperature followed by solidification together near 220 °C, and later crystallisation of some remaining phenothiazine. At fast cooling rates there are usually one or three crystallisation peaks.

Crystallisation at slower cooling rates (2 °C/min) mostly results in two peaks. The first one is the depressed concurrent crystallisation of polyamide-4,6 with phenothiazine under the gentler crystallisation conditions followed by the crystallisation of residual phenothiazine just under the phenothiazine crystallisation temperature. The depression of the first peak with slow crystallisation is proportional to the percentage phenothiazine and can reach a depression of 70 °C for a sample that is 21% polyamide-4,6.

Reheating all these samples leads to thermograms that reverse the crystallisation steps. The temperatures are slightly different as would be expected when involving the crystallisation and remelting of polymers.

There appears to be little interaction between the two materials melting at temperatures below approximately 220 °C although the phenothiazine is at much higher temperatures than its melting temperature and will be at very low viscosity. There are strong interactions at temperatures above 220 °C if the molecules are intimately mixed and not powders or crystallised into separate phases. IR shows no evidence of hydrogen bonding, though.

The repeat melting of blends after cooling quickly at 25 °C/min does not lead to the double main melting peaks found with polyamide-4,6/carbazole. There, the polyamide had been trapped in a metastable form that melted and recrystallised before the melt of the stable form.

At first sight it could be said, in comparison, that there is also little interaction between carbazole and polyamide-4,6 but the carbazole appears to dissolve powders of semi-crystalline polyamide-4,6 more easily than phenothiazine does. There appears to be a basic difference between the two materials in their interaction with polyamide-4,6. We will see in further chapters how the two materials react similarly or differently with the other polyamides being studied and this will be brought together in the final chapter.