

## Chapter 10

### POLYAMIDE-6,12 WITH PHENOTHIAZINE

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#### 10.1 Introduction

Chapter 10 covers the melt blending of polyamide-6,12 and phenothiazine. It is the last of the chapters dealing with experimental trials on small scale melt blending of powders and their DSC investigation and in the making of bulk materials in ampoules plus their investigation with various techniques.

Polyamide-6,12 is an even-even polyamide and has the lowest density of amide groups in the group of four polyamides studied. In principle, it should be the closest to a polyolefin. It does display a low melting temperature consistent with that aspect but the polyamide-6,9 has a slightly lower melting temperature as a result of it being an even-odd polyamide. The melting temperature of polyamide-6,12 is above that of the phenothiazine that it is being melt blended with.

This chapter will show thermal behaviour of polyamide-6,12/phenothiazine blends in pans similar to that seen in the previous chapter with polyamide-6,9/phenothiazine blends. There was one exception compared to all other tests done. One sample had no depression of the phenothiazine crystallisation when cooled quickly.

The maximum depression of the polyamide crystallisation is much less than seen with polyamide-6,12/carbazole and it occurs at 36% polyamide rather than near 75% polyamide-6,12 with the carbazole. The comparisons will be brought together with much more detail in the General Conclusions chapter and that chapter will cover the comparisons between the different polyamides more closely.

## 10.2 Thermogravimetric Analysis

TGA results for samples taken from ampoules are compared in Figure 10-1 with the expected levels for polyamide from the weights of materials used in the ampoules. The TGA results are those for the plateau level at 300 °C after heating the samples at 10 °C/min in a nitrogen gas stream.

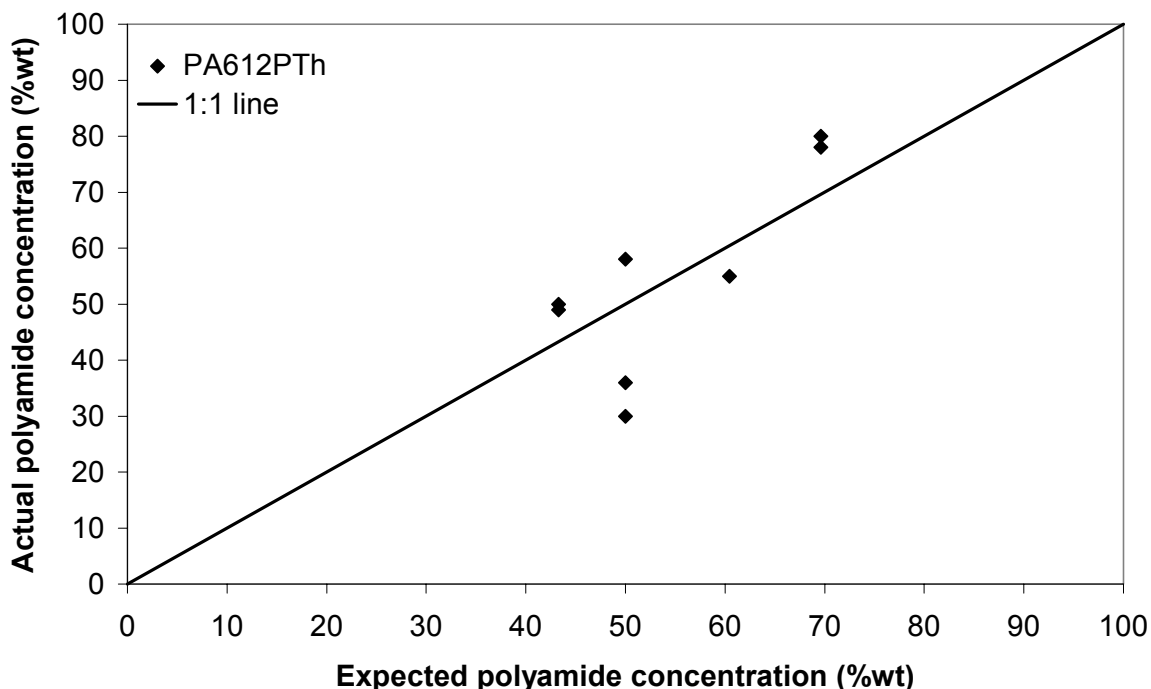


Figure 10-1 Actual vs expected weight percentage polyamide in samples from polyamide-6,12/phenothiazine blends from ampoules. The plateau levels at 300 °C are compared with the percentages from weights of the constituents added to the ampoules for blending.

Some of the data points in Figure 10-1 for ampoule samples show a divergence between the expected and actual concentrations of polyamide in

the samples. These ones are all from early in the trials where the ampoule cooling process had not been fully refined, leading to less consistent polyamide concentration in the ampoule samples. They have been included in the data used for this chapter because they extend the concentration range investigated. There could potentially be some deviations from the general behaviour during the first melting in the DSC because their immediate thermal history has differed slightly.

### 10.3 Differential Scanning Calorimetry

Polyamide-6,12 has a melting temperature in the range 216-218 °C with crystallisation in the range 185-197 °C, depending on the cooling rate and as stated in Chapter 6.

#### 10.3.1 Pan Melt Blending

##### 10.3.1.1 Melting Temperatures for first heating ramp of the powders at 5 °C/min

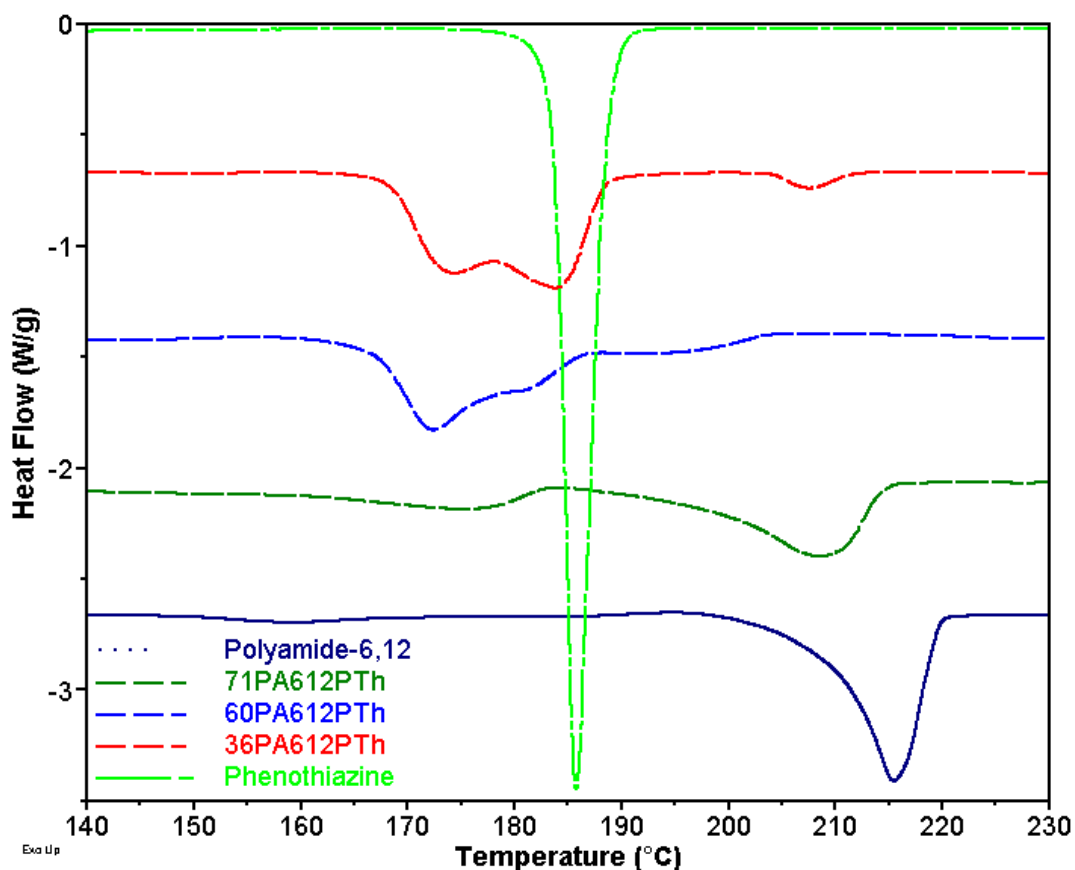


Figure 10-2 DSC thermograms during the first melting at 5 °C/min of polyamide-6,12, phenothiazine and powder mixtures of the two.

The DSC thermograms for the first melting in DSC pans of polyamide-6,12, phenothiazine and three mixtures of the powders at 5 °C/min are shown in Figure 10-2. Similarities will be seen with the polyamide-6,9/phenothiazine combination of Chapter 9.

- a) The polyamide-6,12 is showing a minor endotherm near 160 °C, and an ill-defined exotherm immediately before the main endotherm which peaks at 216 °C. The minor peaks can be better seen in the Appendix A, along with a horizontal line to differentiate exotherms from endotherms. They represent the effects of the thermal history of the sample. The sample is displaying some of the characteristics of granule manufacture, grinding stress and the later thermal treatment during vacuum drying prior to these trials.
- b) The thermogram for 71PA612PTh comprises a broad endotherm over the range 160-180 °C followed by a broad, skewed peak near 210 °C. That first endotherm is the melting/dissolution of some of the polyamide-6,12 with phenothiazine. This is followed by the TLS peak of polyamide-6,12 dissolving into the saturated solution as the temperature nearly reaches the normal polyamide melting temperature.
- c) 60PA612PTh has a thermogram with three peaks, a double peak at 172/183 °C and a very broad weak peak that extends from the double peak to 204 °C. The second peak of the double peak is much weaker and could be a TLS peak of phenothiazine dissolving when considered with the 36PA612PTh thermogram. Alternatively it could possibly be a TLS peak for polyamide-6,12 if raising the temperature above 190 °C places the sample in a part of phase space where polyamide-6,12 has very limited solubility. The very weak broad peak above this is most likely the slow dissolution of remaining polyamide-6,12 into the saturated solution [159].
- d) The thermogram for 36PA612PTh has a double peak at 174/184 °C, 1-2 °C higher than the double peak of 60PA612PTh. The relative heights of the peaks in the double peak are in reverse order with the second now far stronger. The higher level of phenothiazine in this sample combined with the lesser amount of polyamide-6,12 points to the first peak for both samples being the dissolution of available polyamide with phenothiazine to form a saturated solution and the second peak being the TLS peak for the consumption of excess phenothiazine. There is a separate small peak near the polyamide-6,12 melting temperature showing that there was some residual polyamide available to melt. The existence of the small

peak may be due the dissolution being slow from reduced solubility of polyamide-6,12 at the higher temperature, as described for 60PA612PTh.

The set of thermograms for the first melting of powders in DSC pans is showing a similar behaviour to that seen with the polyamide-6,9/phenothiazine blends with a saturated solution of the two materials forming nearly 40 °C below the polyamide melting temperature and approximately 15 °C below the phenothiazine melting temperature when there is at least 35% phenothiazine in the mixture. Excess phenothiazine will only dissolve in the high temperature solution with a TLS peak at elevated temperatures (up to the phenothiazine melting temperature). Some of the polyamide appears to have difficulty in dissolving when the phenothiazine level is high and will only melt at close to the normal polyamide melting temperature.

#### 10.3.1.2 Crystallisation for first cooling ramp of the molten blend at 25 °C/min

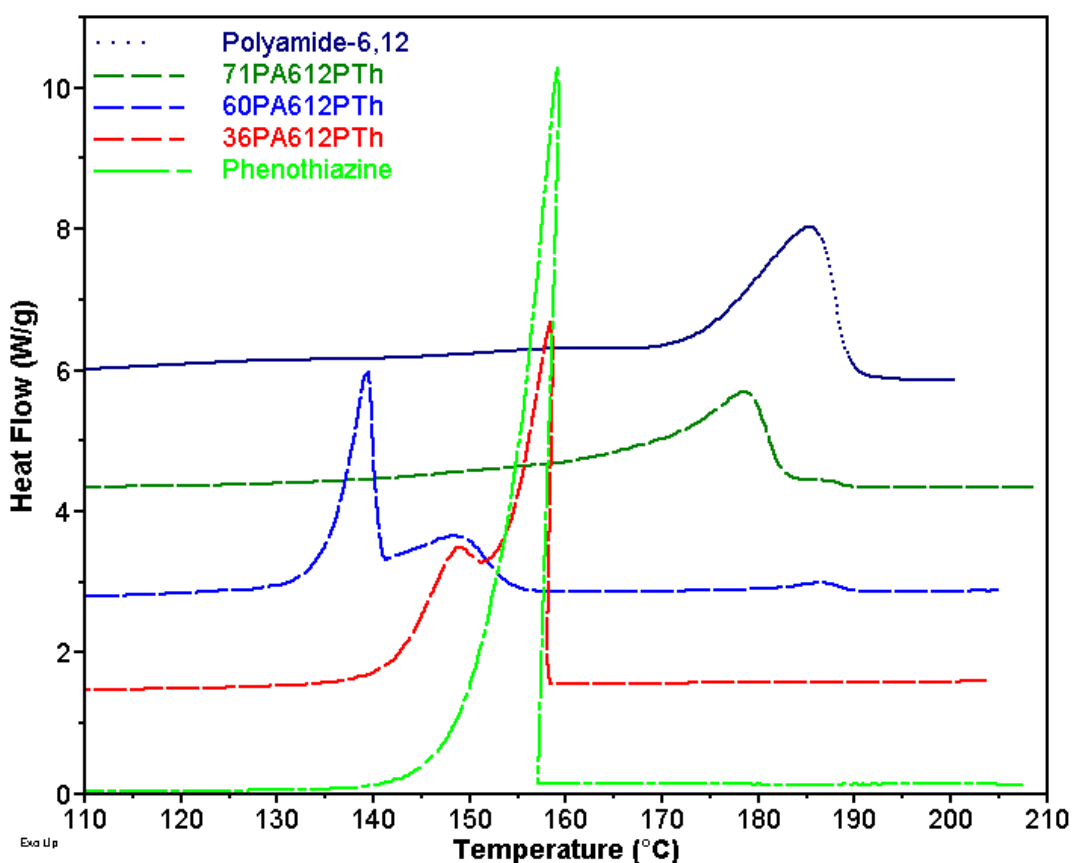


Figure 10-3 DSC thermogram for first crystallisation of pan blended polyamide-6,12/phenothiazine from the melt at 25 °C/min.

The thermograms in Figure 10-3, for the first cooling at 25 °C/min of polyamide-6,12, phenothiazine powders and their mixtures that had been taken to the melt, are described below:

- a) Sample 71PA612PTh has a small crystallisation of nearly pure polyamide ahead of the major peak for the slightly depressed crystallisation of polyamide-6,12. It is noteworthy that the trailing edge of the main peak extends down to approximately 150 °C before petering out but no explanation is available for that.
- b) The thermogram for the 60PA612PTh sample begins, similar to 71PA612PTh, with the crystallisation of a small amount of polyamide-6,12. It is only at 40 °C lower that we see the depressed crystallisation of polyamide-6,12 with phenothiazine in a double peak that changes into the crystallisation of phenothiazine with some polyamide-6,12. The much less “spiky” form of the latter peak is an indication that there is a moderate amount of the polyamide crystallising with the phenothiazine.
- c) The thermogram for the sample 36PA612PTh is unlike the previous two discussed in that there is no crystallisation peak near the normal polyamide-6,12 crystallisation temperature. The thermogram also differs from other crystallisation thermograms seen in previous material combinations in that there is a major phenothiazine crystallisation peak at virtually the same temperature as the pure phenothiazine. In previous thermograms, we have usually seen some depression of major diluent crystallisation by polyamide. This shows that there is virtually no interaction between the two materials in this particular case. The crystallisation is part of a double peak where the phenothiazine crystallisation changes into a depressed polyamide-6,12 crystallisation as the phenothiazine crystallisation progresses. The only exception to this was with the ampoule samples 25PA6Car and 28PA69Car at its first crystallisation where they phase separated and crystallised 1 – 2 °C lower under the differing cooling rate.

This set of thermograms shows some interesting features. With past material combinations we have only seen odd cases where the crystallisation of almost pure phenothiazine changes into the depressed crystallisation of polyamide. We have not previously seen the crystallisation of phenothiazine from a polyamide/phenothiazine solution where the crystallisation takes place at the same temperature as for pure phenothiazine.

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

The DSC thermograms found in Figure 10-4 for the repeat melting at 5 °C/min of polyamide-6,12/phenothiazine samples melt blended previously in DSC pans are discussed below:

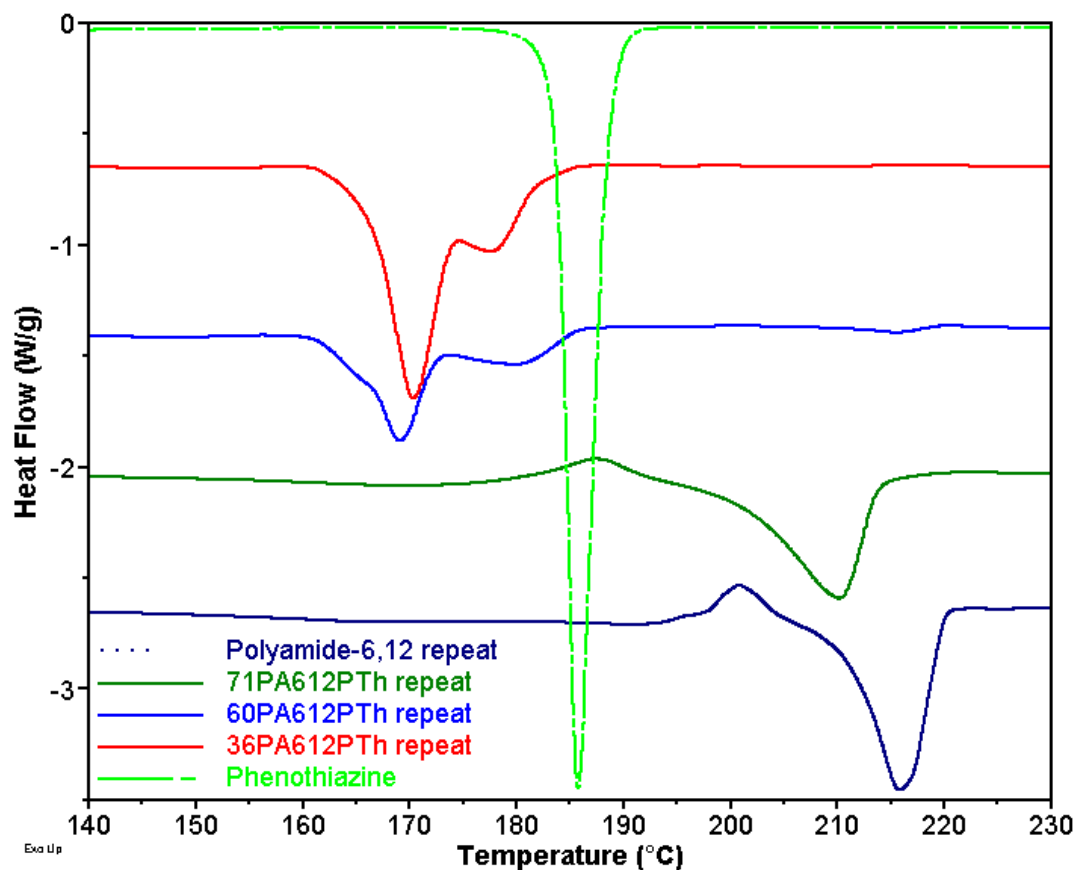


Figure 10-4 DSC thermograms at 5 °C/min for the second melt of polyamide-6,12/phenothiazine materials previously melt blended in pans and crystallised at 25 °C/min.

- The polyamide-6,12 thermogram, where the sample has been remelted after being cooled at 25 °C/min, shows the typical shape of melting of the metastable lamellae followed by recrystallisation into the stable form before undergoing full melting of the stable form. The exothermic peak for the crystallisation rises quite noticeably above the baseline of the thermogram, indicating a substantial drop in free energy by the crystallographic reorganisation.
- The 71PA612PTh sample undergoes the same processes as the polyamide-6,12 but is depressed in temperature because of the phenothiazine present in the sample. The melting/recrystallisation of the metastable form is depressed by 15 °C for this sample but the main melting peak is depressed by less than 10 °C. The tail of the main peak,

overlapping the normal melting region for polyamide-6,12, most likely incorporates the melting of polyamide-6,12 seen to crystallise as near pure polyamide in Figure 10-3.

- c) The 60PA612PTh thermogram shows a treble peak for the melting and dissolution of metastable polyamide-6,12 into a high temperature solution followed by a TLS peak for the dissolution of excess phenothiazine or polyamide-6,12 only at further temperature elevation. There is minor melting of residual, nearly pure, polyamide-6,12 at the normal polyamide-6,12 melting temperature, confirming the previous crystallisation seen in Figure 10-3. The TLS peak could possibly be for either material but two factors point towards it being for the polyamide. Firstly, there is generally a nexus between the concentration for crystallisation of both materials at the same time and the eutectic concentration. We will see at Figure 10-5 in the next section that the crystallisation at the same temperature would be found between 60 and 36% polyamide for the next crystallisation of these samples. It will be found close to 36% from the first crystallisation of the ampoule samples in Figure 10-8. Secondly, the concentration region where the eutectic concentration for ampoule samples lies is between 30 and 50% polyamide-6,12. The eutectic concentrations of pan and ampoule samples were found to be virtually identical for other diluent/polyamide combinations. The connection between eutectic concentration for melting and the concentration where diluent and polyamide crystallise at the same time is also the same for other diluent/polyamide combinations. It therefore seems likely that this TLS peak is for the polyamide because the polyamide concentration is higher than the above ranges.
- d) The initial melting of metastable polyamide-6,12 in the 36PA612PTh sample and recrystallisation before the main melting is not so clearly seen but can be picked out more clearly in Appendix A. The main melting peak is close to that for 60PA612PTh. The process of forming a saturated solution should be nearly the same in both cases, so temperatures of the peaks were close, as expected. Saturated solution formation is followed by a phenothiazine TLS peak.

This thermograms display behaviour expected from previous chapters for remelting polyamide/phenothiazine samples that had been cooled rapidly. That sort of melting of metastable crystalline forms of the polyamide and re-crystallisation was also seen in some of the polyamide/carbazole blends. We have also seen here the remelting at normal polyamide-6,12 melting temperatures of near pure polyamide that was seen to crystallise at near normal crystallising temperatures for the polyamide. That melting of the near-pure polyamide-6,12 lamellae has not happened during the general dissolution of polyamide-6,12/phenothiazine in the eutectic melt so either the polyamide is constrained from melting because it is within a binodal region of phase space or it is resistant to earlier dissolution because it is in a particularly stable lamellar/crystallographic configuration.

#### 10.3.1.4 Crystallisation Peak Temperatures for second cooling at 25<sup>o</sup>C/min

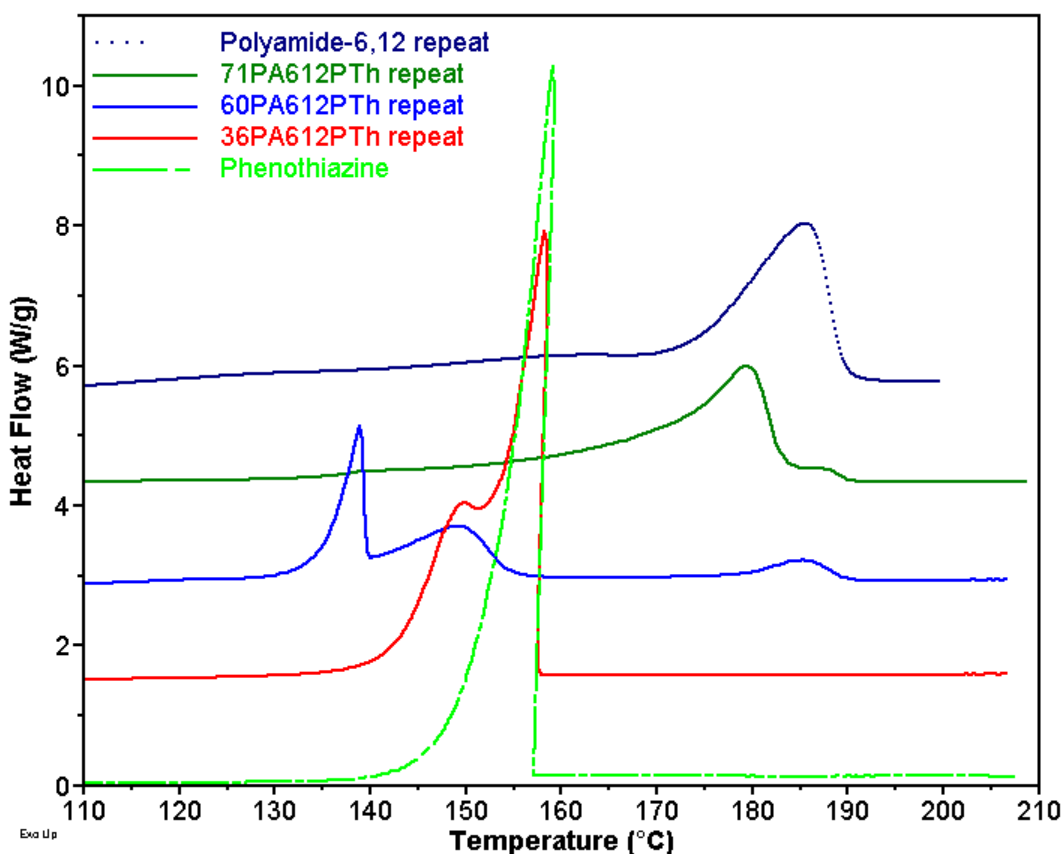


Figure 10-5 DSC thermograms of the second crystallisation at 25 °C/min of pan blended polyamide-6,12/phenothiazine samples.

Figure 10-5 depicts the thermograms for the repeat crystallisation cycle at 25 °C/min of polyamide-6,12/phenothiazine samples originally blended in DSC pans from powder mixtures. They are nearly identical to the first crystallisations, as expected from earlier chapters. The slight differences are

due to the loss phenothiazine in the intervening high temperature heating regimes, resulting in minor polyamide concentration changes in the samples.

### 10.3.2 Ampoule Material

#### 10.3.2.1 Melting Temperatures (First melt in DSC at 5 °C/min)

The DSC thermograms of eight blends of polyamide-6,12/phenothiazine and the raw materials from ampoule samples during the first heating ramp at 5 °C/min are shown in Figure 10-6.

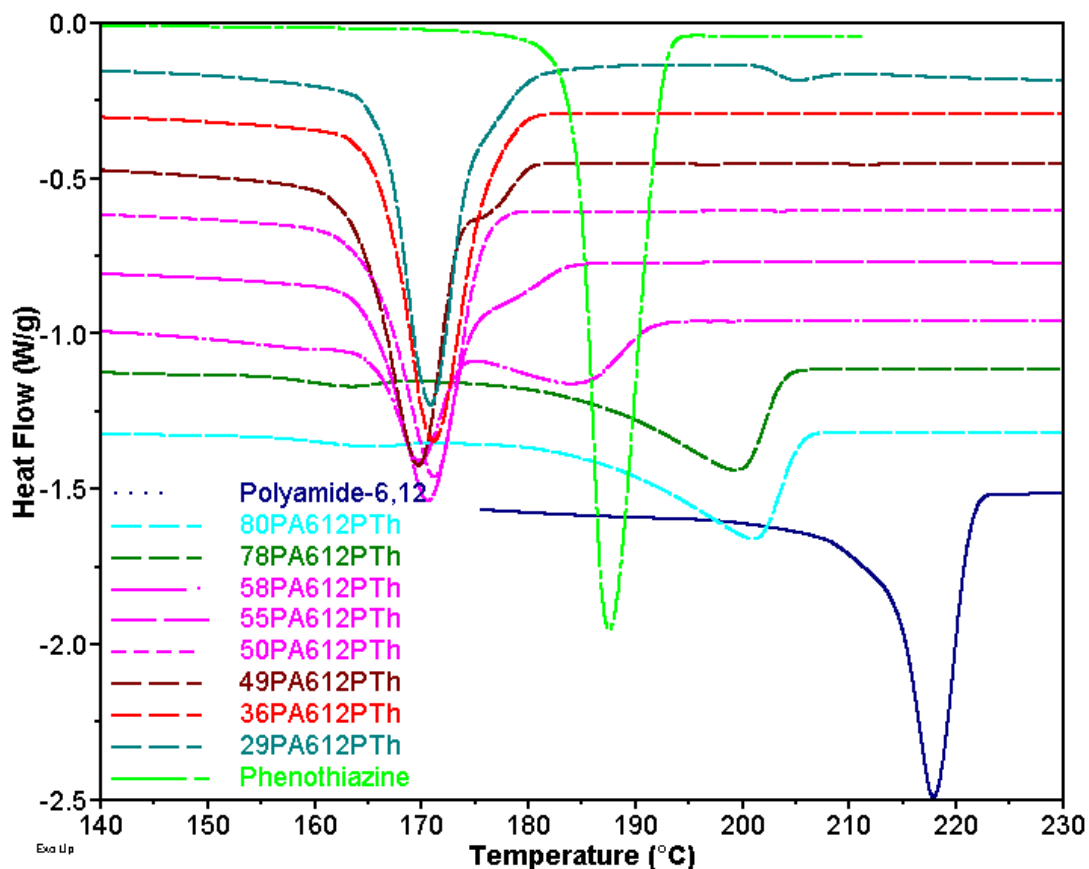


Figure 10-6 DSC thermograms of polyamide-6,12/phenothiazine ampoule samples first melting in the DSC at 5 °C/min.

It should firstly be noted here that the samples 30, 36 and 58PA612PTh were from early ampoules and deviated in the initial cooling from the way the standard process developed later. In particular, the sample 29PA612PTh would have deviated much more than the other two from the standard cooling set-up. The cooling for 29PA612PTh had been done manually which meant that the set-point for the furnace had been set lower by 20 °C every 10 minutes. The result was an undulating cooling ramp averaging 2 °C/min but with steeper sections. That occurred until the thermal mass of the furnace, combined with the smaller temperature difference from ambient, slowed the cooling rate right down to a minimal rate. The results are

included here to give a broad picture of the likely thermal responses in the DSC, but obviously with some caution. The large set of thermograms here will be treated together to minimise repetition.

The two samples near 80% polyamide have skewed main peaks after a weak endotherm near 165 °C. This weak endotherm can be seen as the process of melting/dissolution of phenothiazine with polyamide-6,12 to form a saturated solution at those temperatures. This is followed by the TLS peak for the remaining polyamide-6,12.

The peak temperatures of the remaining samples lie closely together in a 2 °C range near 170 °C. They represent the eutectic melting temperature of the polyamide-6,12/phenothiazine blends. Slight differences in the temperature had also been seen with the pan blended samples. The other curves are followed by smaller TLS peaks as samples with less polyamide-6,12 are taken until the TLS peak for polyamide-6,12 disappears near either 50 or 35% polyamide. There are some minor exceptions in the whole set of curves but there is a strong trend to support this notion.

We see the lead-in to the main peaks do not show the melting/re-crystallising of metastable polyamide. The absence was expected from the slower cooling rates employed with the ampoules.

The 29PA612PTh sample has a small peak at the polyamide-6,12 melting temperature but just from this thermogram it is not known if this is due to the slightly different cooling that had occurred with this sample during formation in the ampoule. We will see in the section on crystallisation in the DSC that a small portion of the polyamide crystallises out during cooling. This minor feature of the thermogram is thus not due to the original semi-controlled cooling regime for that sample in the ampoule but due to the temperature/concentration conditions the sample is experiencing.

#### *10.3.2.2 Overall Crystallinity*

The overall crystallinity is plotted in Figure 10-7 for the series of ampoule samples taken to the melt in the DSC. We see a generally decreasing level of crystallinity for higher and higher concentrations of polyamide-6,12 in the figure.

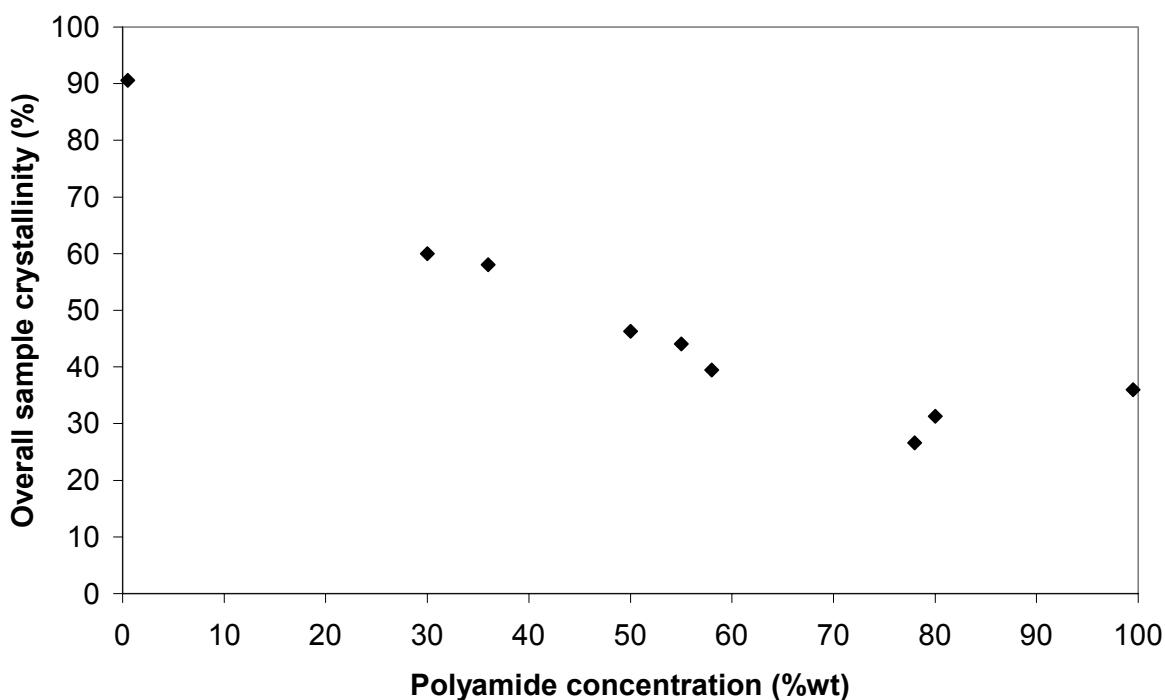


Figure 10-7 Overall crystallinity determined from the first DSC melting enthalpy of polyamide-6,12/phenothiazine ampoule samples and TGA vs weight percentage polyamide from TGA plateau level at 300 °C.

The level of crystallinity at approximately 80% polyamide actually dips slightly below that of the polyamide. The lack of a linear relationship proportional to concentration shows that the crystallinity of blends is being suppressed overall by the melt blending process.

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

Figure 10-8 shows the thermograms of the crystallisation of material melt-blended in ampoules, taken to the melt in the DSC and then crystallised for the first time in the DSC at 2 °C/min.

This set of DSC thermograms for the first cooling ramp of the ampoule samples in the DSC will be treated as a whole, as with the first melting of ampoule samples in the DSC. The alignment of the thermograms from highest downwards to lowest concentration of polyamide in the samples makes it clear that there are several processes taking place in the series of thermograms.

The 29PA612PTh thermogram is the only one to have crystallisation of nearly pure polyamide-6,12 with the exception of the 55PA612PTh sample having a very faint broad exotherm in that region. The exotherms are due to

a small amount of the high temperature solution beginning to phase separate.

There is an increased depression of the polyamide crystallisation with lower polyamide levels in the blend. That occurs down to the 36PA612PTh sample, where the crystallisation starts as a phenothiazine crystallisation and changes into (highly depressed) crystallisation of the polyamide-6,12 within the same peak.

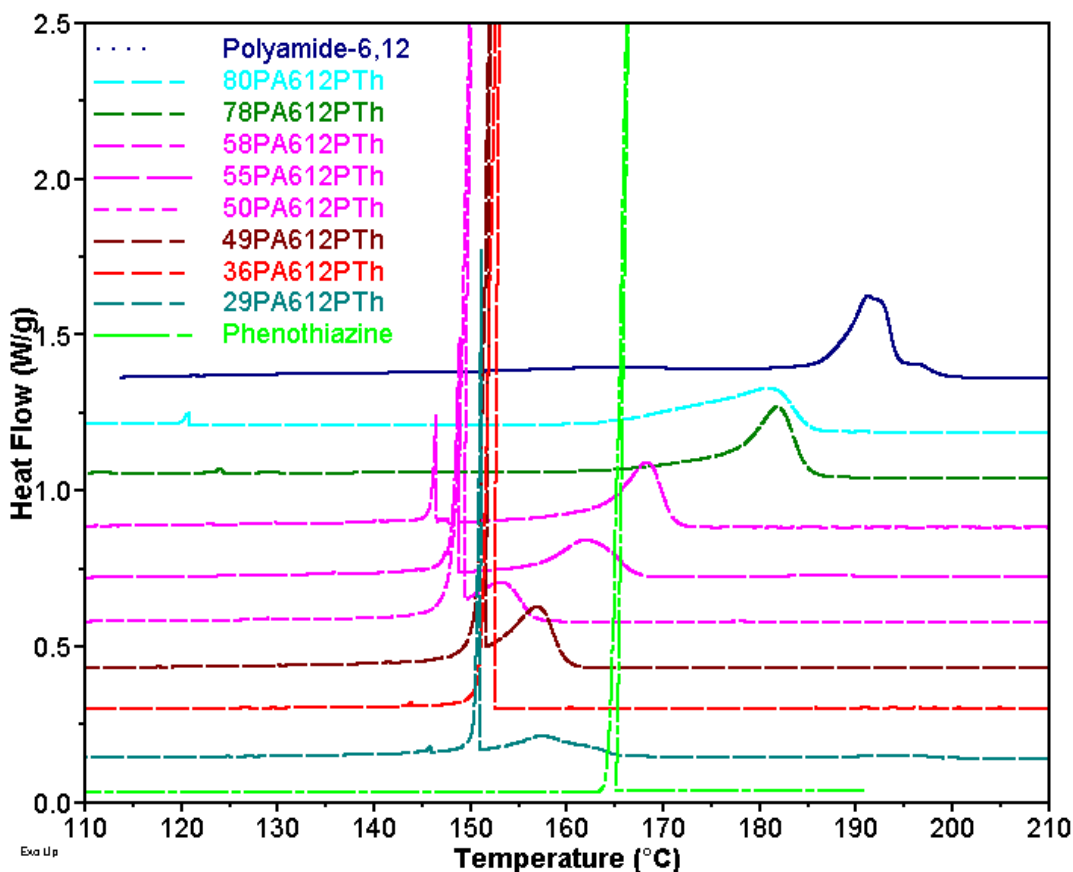


Figure 10-8 DSC thermograms of the first crystallisation in the DSC at 2 °C/min of polyamide-6,12/phenothiazine ampoule material.

The 29PA612PTh sample has a polyamide peak at higher temperatures than the 36PA612PTh sample so there appears to be a maximum in the polyamide-6,12 crystallisation temperature depression, as was found with ampoule samples for polyamide-6,9/phenothiazine in Chapter 9. A minimum of the polyamide crystallisation was not found with the other polyamide/diluent combinations, possibly, in some cases because sufficiently low polyamide concentrations were not explored and in others because the diluent crystallised first. The peak near 155 °C for 29PA612PTh incorporates a small sub-peak on the leading edge but the form is Gaussian

rather than the “spiky” peak of phenothiazine crystallisation. The reason for that shoulder peak is unknown at this stage.

“Spiky” peaks for the crystallisation of quite pure phenothiazine can be seen depressed progressively less as the level of polyamide is reduced. At 58% polyamide-6,12 there is strong crystallisation of phenothiazine depressed by 18 °C from the normal phenothiazine crystallisation temperature. The temperature that the crystallisation occurs at and the size of the peak increase as the level of polyamide is reduced further until there is a 10 °C depression for the 36PA612PTh sample. The last thermogram, at 29% polyamide does actually have a slightly higher depression of the phenothiazine crystallisation by 2 °C.

There are also small secondary phenothiazine crystallisations at lower temperatures than the main phenothiazine crystallisation peaks with this polyamide/diluent combination. They are the crystallisation of residual domains of phenothiazine as far down as 120 °C, some 45 °C below the normal phenothiazine crystallisation temperature under these cooling rates. The amounts of material involved in these cases are of the order of 5 to 10 µg in a 10 mg sample. The secondary crystallisations are from small pockets where the mobility of the phenothiazine through the thickening amorphous polyamide is still sufficiently high that a few molecules can group. They can then crystallise into a phenothiazine micro-domain before the viscosity drops too far and they become individually trapped in the amorphous region.

The large number of ampoule samples spanning a wide range in polyamide concentration in this data give a good opportunity to see overall trends taking place. The generally increased depression of polyamide crystallisation with increased concentration of phenothiazine and the increased depression of the main phenothiazine crystallisation temperature with increased polyamide concentration can quite clearly be seen and both show the Flory-Huggins style interaction between the materials.

Interest in the different behaviour of the 29PA612PTh sample with respect to the others should be tempered by the knowledge that the ampoule was originally made in a different manner to the others. This different behaviour would have to be confirmed by other ampoule samples made with similar concentrations of polyamide-6,12 under standard furnace conditions.

### 10.3.2.4 Crystallinity from first crystallisation in the DSC

The crystallinity of phenothiazine and polyamide is displayed in Figure 10-9 from the first cooling ramp in the DSC.

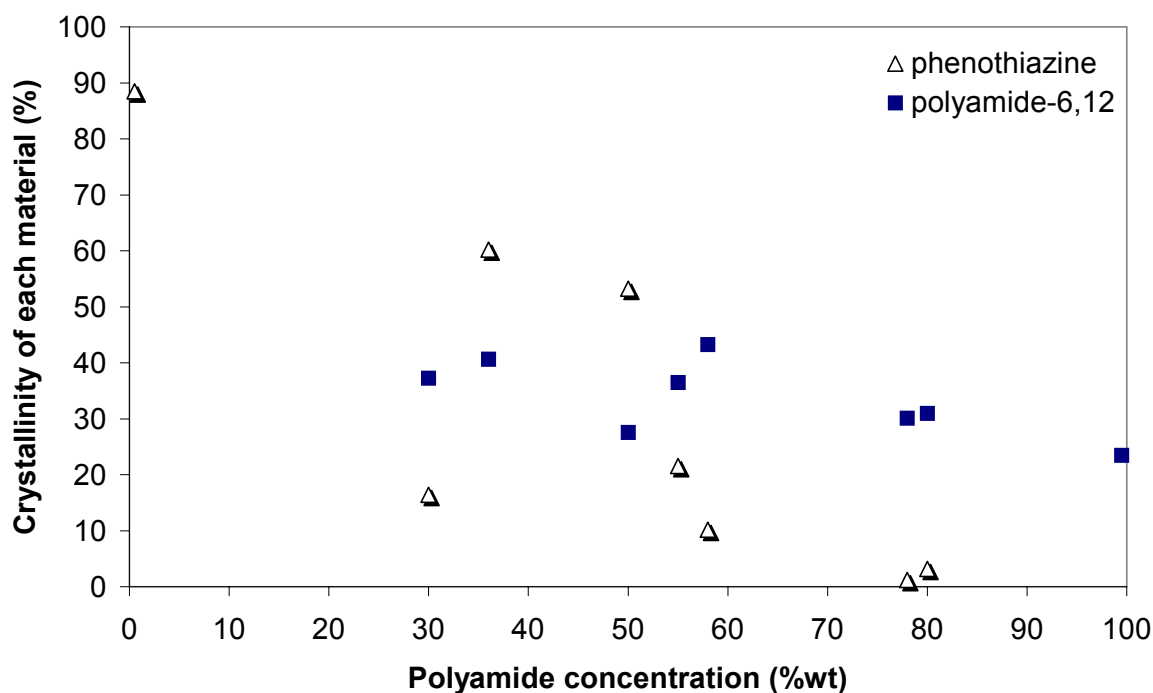


Figure 10-9 Crystallinity of Phenothiazine and Non-Phenothiazine parts from the first crystallisation of polyamide-6,12/phenothiazine ampoule samples from the melt at 2 °C/min in the DSC versus weight percentage of polyamide-6,12.

The crystallinity of the phenothiazine, as with the crystallisation depression, is very variable but reduces to zero by 80% polyamide-6,12. It is another example of the scatter in the phenothiazine enthalpy of crystallisation seen with polyamide/diluent combinations having a higher polyamide than diluent melting temperature.

The crystallinity of the non-phenothiazine portion gradually increases to 40% as the level of polyamide is reduced.

### 10.3.2.5 Phase Diagram from first heating and cooling ampoule material in DSC

The phase diagrams in Figure 10-10 are similar to those of previous chapters where the polyamide normally crystallises at higher temperatures than the diluent. The only difference here is that there is an upturn at low polyamide concentration so that the polyamide crystallises before the diluent below 35% wt of polyamide. The first melting is at near-constant temperature implying a eutectic.

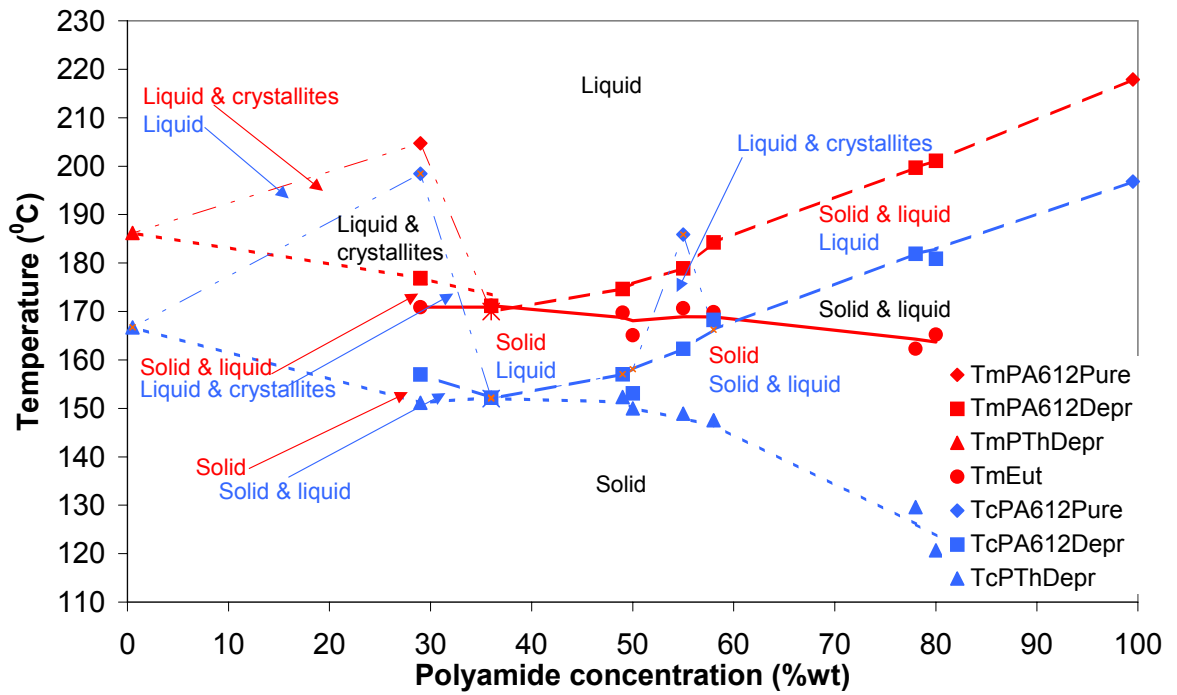


Figure 10-10 Non-equilibrium phase diagrams for polyamide-6,12, phenothiazine and their blends with Flory-Huggins style melt/crystallisation depressions.

### 10.3.2.6 Third Melting of materials/Second DSC Melt

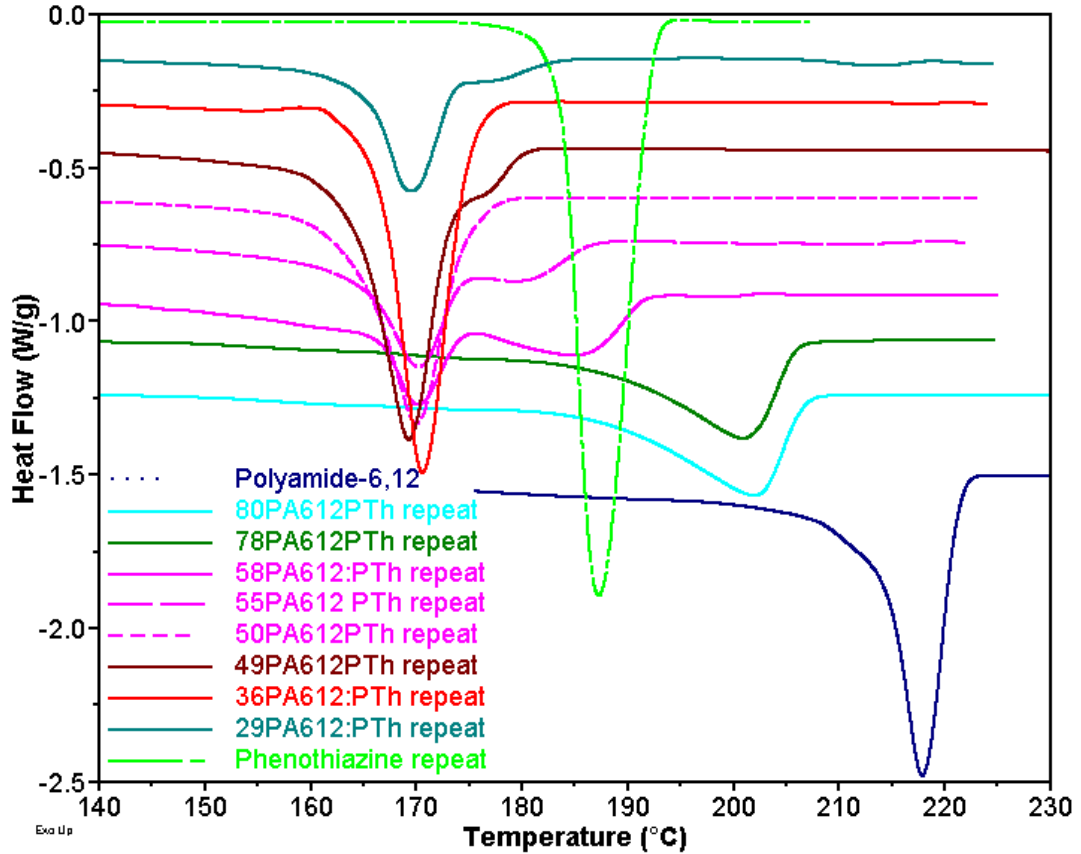


Figure 10-11 DSC thermograms of the second melt at 5 °C/min in the DSC of polyamide-6,12/phenothiazine ampoule material.

The ampoule samples in pans from the first DSC runs were passed through a repeat melt/crystallisation cycle in the DSC as was done in earlier chapters. Figure 10-11 below shows the DSC thermograms of the melting portions of the repeat DSC runs made at 5 °C/min heating rate for ampoule samples.

Generally, the trends in this set of thermograms are similar to those seen in the first melt. The differences that can be seen can be attributed to the loss of some phenothiazine due to evaporation. This can be seen, for example, with some smaller main peaks and larger TLS peaks, indicating a move in the direction of increased polyamide concentration in the samples. There is some reduction in crystallinity with a few of the samples, most notably the 29PA612PTh sample. That sample had originated from early ampoule trials. Differences from the first melting may not be fully representative because we are now looking at the crystallinity embodied from a proper 2 °C/min cooling rather than the crystalline state after a partly uncontrolled cooling.

#### 10.3.2.7 Third Crystallisation of Materials/Second DSC Crystallisation

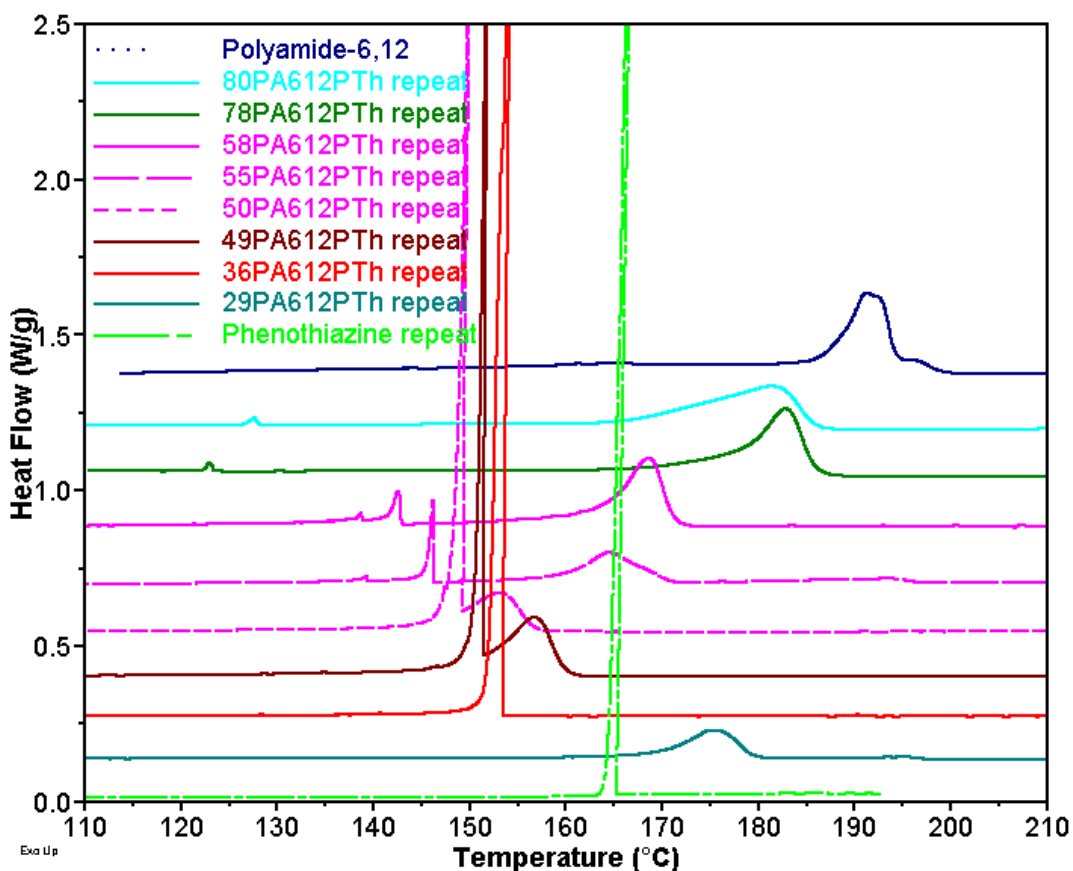


Figure 10-12 Thermograms of the second crystallisation at 2 °C/min in a DSC of polyamide-6,12/phenothiazine ampoule material.

The set of thermograms seen in Figure 10-12 for the second DSC crystallisation of ampoule samples of polyamide-6,12/phenothiazine blends are generally similar to the set in Figure 10-8 for the first crystallisation.

The small differences that can be seen are due to the evaporation of phenothiazine. The exception to this is the 29PA612PTh sample where the phenothiazine crystallisation peak has disappeared and the main peak has moved higher by 15 °C. The crystallisation peak of nearly pure polyamide-6,12 remains. Again, with this material combination we see some very small spiky peaks below the main peaks where extremely small amounts of phenothiazine are crystallising in ampoule samples.

#### **10.4 Fourier Transform Infrared Spectroscopy**

Samples from all the ampoules made with polyamide-6,12/phenothiazine blends underwent FTIR with photoacoustic detection in the mid range IR and again with DRIFT in the Near Infrared region. In no case was there any evidence of hydrogen bond interactions between the polyamide-6,12 and the phenothiazine. Results may be seen in Appendix D on CD.

#### **10.5 Summary**

There are similarities with the polyamide-6,9/phenothiazine blends made in DSC pans during the first melting. Melting/dissolution of polyamide-6,12 occurs here in a saturated solution with phenothiazine approximately 40 °C below the polyamide melting temperature. This is followed by the dissolution of excess polyamide or phenothiazine with a TLS peak at temperatures below the respective normal melting temperatures. Some of the polyamide-6,12 appears to have difficulty in dissolving into the saturated high temperature solution until the normal polyamide melting temperature is reached as with the polyamide-6,9. This is confirmed during crystallisation by the tendency of polyamide-6,12 to crystallise out when cooled at 25 °C/min.

One aspect found with the fast crystallisation in pans with this material combination, and not found elsewhere in the thesis, is the crystallisation of phenothiazine in a blend (36PA612PTh) without any crystallisation temperature depression for the phenothiazine. That is indicating a less favourable interaction between polyamide-6,12 and phenothiazine under those conditions.

The remelting of those samples crystallised quickly shows an initial melting/recrystallisation of the metastable form of the polyamide into the stable form prior to the main melt. That behaviour has been seen previously with other polyamides in blends with both carbazole and with phenothiazine.

Blends made in DSC pans and remelted showed temperature limited solubility of phenothiazine in mixtures with 60% polyamide and less.

The range of ampoule samples available for polyamide-6,12/phenothiazine blends allowed clear trends to be seen in the melting temperature limited solubility peaks and crystallisation temperature depression of the samples. In particular, the depression of polyamide crystallisation by the phenothiazine and the depression of phenothiazine crystallisation by the polyamide-6,12 was very clear.

The behaviour of polyamide-6,12/phenothiazine blends differs from that with polyamide-6,12/carbazole blends in that the maximum depression of polyamide crystallisation is now 40 °C rather than the 60 °C seen with carbazole. In this case, the maximum depression is seen at 36% polyamide rather than near 75% polyamide.

The melt blending of polyamide-6,12 with phenothiazine has been investigated by FTIR in two spectral regions with differing detection systems and found not to involve hydrogen bond interactions between the two materials. This is the same result as has been found for all combinations of the four polyamides studied with either carbazole or phenothiazine.

The similarities and differences between the blending of each of the four polyamides with carbazole and with phenothiazine will be covered fully in the chapter on General Conclusions that follows.