

GENERAL CONCLUSIONS

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The thesis has explored the melt blending of four different aliphatic polyamides with each of two small molecule organic diluents. In conjunction with this, their solidification at different cooling rates were investigated. The polyamides studied were polyamide-4,6, polyamide-6, polyamide-6,9 and polyamide-6,12, representative of a range of amide densities and polyamide types. The resulting combinations of melting temperatures of the polyamides and the diluents, carbazole and phenothiazine, allow conclusions to be made about the effects of relatively mobile diluent molecules on the crystallisation processes. The range of polyamides studied also allows further conclusions to be made about the effects of polyamide repeat structure on eutectic compositions and maximum crystallisation and melting depressions.

11.1 Thesis arguments

11.1.1 Effects of relative crystallisation temperatures

The main differences in morphology resulting from crystallisation processes at the relatively slow cooling rate of 2 °C/min are related to whether the crystallisation temperature of the polyamide is higher or lower than the diluent. The combinations PA46PTh, PA46Car, PA6PTh, PA612PTh and

PA69PTh all have a polyamide crystallisation temperature greater than the diluent to varying degrees. In contrast, the group PA6Car, PA612Car and PA69Car have a polyamide crystallisation temperature lower than the diluent.

The group with polyamide crystallising above the diluent are all characterised by crystallisation depression phase diagrams demonstrating:

- a) Some possibility of a small amount of crystallisation within 10-15 °C of the normal polyamide crystallisation temperature.
- b) Major near-Gaussian crystallisation peaks at increasingly lower temperatures as the level of polyamide in the blend is reduced.
- c) Major “spiky” style crystallisation peaks for the diluent at increasingly lower temperatures as the level of the diluent in the blend is reduced.

These characteristics can be seen for the first DSC crystallisations of ampoule material in Figures 3-13, 3-19, 7-8, 8-8, 9-8 and 10-8 plus their second crystallisations in the DSC and stand out more clearly in the relevant phase diagrams in Figures 3-22, 7-10, 8-10, 9-10 and 10-10 where transition temperatures are plotted directly against concentration. In some cases there is a minor variant in the polyamide crystallisation, where the depression of the peak is greatest at the point where polyamide and diluent crystallise at virtually the same time. This polyamide crystallisation temperature depression is often not so great at lower polyamide concentrations. Examples of a minimum in polyamide crystallisation temperature for the two materials crystallising at the same time are seen in Figures 9-8 and 10-8 or the phase diagrams Figures 9-10 and 10-10. These characteristics can also be seen in samples melt blended in pans and cooled at 25 °C/min, although more crystallisation occurred near the polyamide crystallisation temperature. This pattern can clearly be seen in Figures 3-6, 7-3, 8-3, and 10-3. The pan blended samples for PA69PTh are not quite so obviously of the same mould due to large evaporative loss with 39PA69PTh and some other minor differences. This increased crystallisation at the polyamide crystallisation temperature is due to the lowered viscosity combined with rapid cooling giving a deeper supercooling to drive the crystallisation. This temporarily allowed more crystallisation before the increase in viscosity at low temperatures brings crystallisation to a halt.

The melting behaviour for this group have phase diagrams that display nearly constant first transition temperatures as polyamide concentration is varied and appear to be eutectic melting.

The above is in stark contrast to the crystallisation characteristics for the group with a polyamide crystallisation temperature less than that of the diluent. The crystallisation for PA6Car, PA69Car and PA612Car was characterised by eutectic types of phase diagrams, Figures 4-13, 5-10 and 6-10, showing:

- a) Little depression in the crystallisation temperature of the diluent until polyamide concentration was raised to 20-30% and then dropping rapidly. There was no crystallisation of diluent at temperatures below that of the polyamide.
- b) There was almost no crystallisation at the polyamide crystallisation temperature.
- c) There was a lower Gaussian peak at a virtually constant temperature, although this was sometimes slightly lower at the concentration where the diluent was crystallising concurrently.

There was no evidence during crystallisation of a peak at eutectic temperatures for polyamide levels higher than the eutectic concentration. The further depression at the eutectic concentration appeared to be of the same nature that Berghmans noted [135 p. 219] (apparent eutectic temperature depressed by non-equilibrium conditions).

Results from the fast cooling used for pan blended samples were consistent with the above results except that a very small amount of crystallisation was often encountered at the polyamide crystallisation temperature when the diluent concentration was very high.

Melting transitions for these ampoule samples can be seen in the phase diagrams to be virtually the same as the crystallisation transitions but occur at 10-25 °C higher temperatures

Further evidence of marked differences between the two groups is in the enthalpy of crystallisation for blends, in regards to the calculated “crystallinity” of the diluent. It can be seen in Figures 3-20, 7-9, 8-9, 9-9 and 10-9 that there were high values of diluent crystallinity at certain

concentration values and low values only a few percent different in concentration, producing a scattered result for diluent crystallinity.

The corresponding figures for PA6Car, PA69Car and PA612Car (Figures 4-12, 5-9 and 6-9) follow a much more regular pattern with a linear drop-off in diluent crystallinity from the very high values for pure diluent to zero at some concentration. This linear drop-off appears similar to those found in van der Heijden's thesis [7]. It is difficult to compare these results due to the differences in focus. He dealt with liquid-liquid phase separation and with an amorphous polymer whereas I used a true monotectic with liquid-solid phase separation, although semicrystalline polyamides are obviously also semi-amorphous.

The above evidence shows that different morphologies will result from quite different crystallisation processes taking place depending on the relative crystallisation temperatures of polyamide and diluent. The reasons for the two sets of morphological behaviour are linked to the very different molecular condition of the two types of material.

Firstly, we should look at the crystallisation of the pure materials. The diluent by itself will normally lose entropy sharply as the small molecules in the molten material rapidly stack themselves into crystals with little hindrance from other molecules. Being small molecules, they have a low viscosity, particularly in the energetic state at the elevated temperatures involved in this study. In contrast, polymers are severely restricted in their ability to crystallise because the long chains must act co-operatively under strong driving forces in order to achieve partial crystallinity. The Olmsted group [30] concluded that the formation of crystallites only takes place after precursor liquid-liquid decomposition of denser, more organised, domains. Thus, slower crystallisation only takes place at much larger supercooling than experienced with small molecules. Crystallisation of polymer chains is also hindered by the limited mobility of the surrounding and entwined non-crystallising chains, which rapidly lose their mobility as the temperature is reduced. It is important to remember that even highly crystallisable polymers are semi-amorphous and this research dealt with a two-phase system in the solid state when considering just the straight polymers. This issue is discussed later in further detail.

The study here concerns polyamides that have considerable hydrogen bond linkages. The effects for the solid material are well known: high melting temperatures caused by the lamellae being linked more solidly together at a chain-to-chain level and the surrounding amorphous material not dropping in viscosity so quickly as the temperature is raised to the melt. The situation above the melt and for cooling is also strongly affected by the hydrogen bonding. There is a high viscosity just above the melting temperature because of the linkages forming and reforming, even if the residence time of the bonds is short. The chains are being pulled strongly by the hydrogen bonds into crystalline lamellae as the temperature drops to the crystallisation temperature. They are restricted more in that action if there is a partial mismatch requiring contortions of the chain backbone to line up the hydrogen bonds (resulting in lower crystallisation temperatures as with polyamide-6,9). The viscosity of the amorphous melt is high and rapidly increasing as the temperature is reduced.

Consider now the situation with a molten blend having two dissimilar crystallisable polymers. There are different possible outcomes. We may have liquid-liquid phase separation before one and then the other type of domain crystallises. Otherwise we will have the higher melting polymer attempting to crystallise first as the temperature of the high temperature solution is reduced if the polymers are sufficiently compatible in the melt. The first material crystallising will attempt to expel the other from the lamellae into the interlamellar region and will crystallise at a lower temperature than normal (higher driving force required). The second crystallising polymer will be in a non-crystallising state at that time and will act as a highly viscous diluent having problems in 'moving out of the way' because of the co-operation needed in moving the long chains. Eventually the second material will crystallise in the interlamellar space or outside the spherulites if it has been able to move far enough away [160]. This sets the framework for a description of the two cases being studied here where there is either a polymer with high crystallisation temperature and diluent with lower crystallisation temperature or the reverse.

Three characteristics of the diluent are that it is highly crystallisable, it will be highly mobile and that it will be either partially compatible or

non-compatible with the polyamide at a molecular level. It will initially act as a plasticiser of the amorphous portion of the semicrystalline solid at low diluent concentrations and become a solvent at high concentrations. We will now look at the expected crystallisation process in different circumstances:

- a) *Polyamide crystallisation temperature higher than diluent and a high polyamide level.* Some samples exhibit only a little crystallisation at the normal polyamide crystallisation temperature. The dynamic cooling used means that there is interplay between the increased supercooling and the reduction in mobility of the diluted polyamide at lower temperatures. The limited or no crystallisation in these situations is related to the kinetics involved. The presence of some crystallisation at the polyamide crystallisation temperature could be due to either of two possibilities. The viscosity of the normally viscous polyamide melt may be reduced by the diluent, allowing easier crystallisation of the polymer chains despite the presence of “foreign” material. Alternatively, there could be some minor phase separation beginning between the two materials, driving the polyamide into a condition more amenable for crystallisation. This would be in a manner similar to the single-polymer phase separation in the melt prior to actual crystallisation of Olmsted *et al* [30]. There are some cases such as in Figure 3-19 where crystallisation temperature has been raised and is possible even above the normal polyamide crystallisation temperature.

In this group of polyamide/diluent combinations we see depression of both polyamide and diluent by each other in the manner of a Flory-Huggins interaction during crystallisation. We have dilution in solution as the major factor suppressing the (possibly second) polyamide crystallisation at high polyamide levels and temperatures well below the normal polyamide crystallisation. The formation of polyamide lamellae in the amorphous polyamide/diluent at temperatures possibly well above the diluent melting temperature may lead to complete expulsion of diluent from the interlamellar region due to its high mobility. Alternatively, some of the diluent may still reside in the interlamellar regions and later lead to a very retarded crystallisation of small

amounts of diluent, or no crystallisation. The remaining diluent would reside in the amorphous polyamide/diluent at lower temperatures.

We see little or no crystallisation of diluent at polyamide levels greater than 75% polyamide. Here, the polyamide crystallisation is being slightly delayed and, in the cases of polyamide-6, polyamide-6,9 and polyamide-6,12 with phenothiazine, the crystallinity of the polyamide portion of the blend is enhanced. This is possibly due to a lowered viscosity of the melt by the diluent at these lower temperatures, leading to easier alignment of polymer chains into a crystallisable condition under the high driving force of greater supercooling. The reason for the apparent randomness of diluent crystallinity has no clear explanation.

- b) *Polyamide crystallisation temperature higher than diluent and a high diluent level.* The comments regarding crystallisation at the polyamide crystallisation temperature are also applicable here.

Slightly suppressed crystallisation of the diluent takes place first (if there has been no minor crystallisation at the polyamide crystallisation temperature). This is due to the presence of a few polymer chains restricting the ability of the diluent to crystallise. The polyamide crystallises later amongst the diluent crystallites. The reason for the slightly lesser crystallisation depression at polyamide concentrations below the point where both crystallise together is not fully understood. It may possibly be related to the above earlier diluent crystallisation shifting the concentration of polyamide in the remaining material to higher levels.

- c) *Polyamide crystallisation temperature lower than diluent and a high polyamide level.* The only guidance on slow crystallisation for these conditions is the one sample, 89PA6Car. That sample crystallised towards the high end of a normal polyamide-6 crystallisation. At that point the small amount of diluent in the sample was already more than 30 °C below its normal crystallisation temperature.

- d) *Polyamide crystallisation temperature lower than diluent and a high diluent level.* Blends in this category have all the hallmarks of concentration dependence of the diluent crystallisation for being a liquid-solid phase separation, ie. monotectic. This process is followed at

a relatively constant temperature by a eutectic-like crystallisation. In this case, excess diluent to the eutectic solution is rapidly crystallised, the eutectic reaction takes place at the eutectic temperature and remaining diluent-infused amorphous polyamide solidifies. The low temperatures of this liquid at the eutectic temperature and the large supercooling of the diluent probably mean that some diluent crystallises at the same time as the polyamide, and most likely in the interlamellar regions. We have noted in the various chapters that crystallinity of the polyamide often appears to be enhanced for this group in the region where the diluent is in excess. Part of that excess may well be the concurrent crystallisation of some diluent.

The almost linear drop in diluent enthalpy of crystallisation with increasing polyamide concentration has some parallels to the results of van der Heijden, although he worked with a non-crystallisable polymer. Zero crystallinity is reached at the Berghmans Point where liquid-liquid phase separation meets the Kelley-Bueche line for glass transition with dilution. The situation here is liquid-solid phase separation with a crystallisable polymer.

The major mediator in the morphology of polyamide/diluent melt blends with carbazole or phenothiazine as the diluent is the relative crystallisation temperatures of the two components. Cases with the polyamide having a greater crystallisation temperature lead to a combination of Flory-Huggins style of crystallisation depressions for each material by the other with possible crystallisation of some polyamide before this. Systems with a higher diluent crystallisation temperature and excess diluent lead to liquid-solid phase separation of the diluent followed by a eutectic-like crystallisation of polyamide (perhaps with some diluent), leaving residual diluent uncrystallised in the amorphous remainder.

11.1.2 Effects of polyamide repeat unit

Three of the four polyamides studied, polyamide-6, polyamide-6,9 and polyamide-6,12 have melting temperatures within a 12 °C range in between the melting temperatures of carbazole and phenothiazine but have quite different repeat unit structures. One is a polyamide-n type and the others are even-odd and even-even polyamide-m,n types, respectively. There are

some differences between these three polyamides regarding melting and crystallisation depressions and concentrations.

The melting temperature depression for ampoule samples is 50 °C for PA6PTh but 29 °C for PA69PTh with respect to the polyamide and 22 °C for PA612PTh but 14 °C for PA6PTh and PA69PTh with respect to the phenothiazine.

The best estimate of molar concentration for the eutectic melting temperature varies for these ampoule samples from 46% polyamide for PA6PTh to 30% polyamide for PA612PTh.

During the first DSC crystallisation of ampoule samples we found that there was a slight amount of crystallisation at the polyamide crystallisation temperature for PA6Car but none for PA69Car or PA612Car. For those types, the eutectic-like crystallisation peaks are depressed by 11 °C for PA69Car but by 21 °C for PA612Car.

The weight percentage polyamide for eutectic crystallisation of ampoule samples varies between 75% for PA6Car to 70% for PA612Car and this becomes 81 and 56% respectively when calculated on a molar basis.

The closest approximation to the work here regarding the effects of polyamide type is perhaps the research of Kim, Char and Kim [10 Fig.4]. They studied, amongst other things, PEG with a 400 Dalton poly(ethyleneglycol) melt blended with polyamide-6, polyamide-11 and polyamide-12. Their work uses a polymer as a diluent, and one that does have hydrogen bonding with the polyamides. They had the (even) polyamide-12 with longer aliphatic chains between the amide groups where, here, we had the even-even polyamide-6,12 with longer chains between some of the amide groups. They also used the (odd) polyamide-11 (melting at a lower temperature than polyamide-12 because of the less favourable chain configuration for hydrogen bonding), similar to the situation for polyamide-6,9. In their case the liquid-liquid phase separation is in the order polyamide-11, polyamide-12, and polyamide-6 with increasing polyamide level whilst the best estimates of eutectic compositions for the three here are greater than 64% for polyamide-6,9, 70% for polyamide-6,12 and 75% for polyamide-6. The comparison could well be there but the approximations are large.

There is a wide range of these types of differences between the behaviour of the different polyamides blended with either carbazole or phenothiazine and cooled at a slow or fast rate. The differences go further than what could be expected from the slight melting temperature differences. It is concluded that they are related to the polyamide repeat unit structure, although the mechanisms are not currently understood.

11.2 Overall common relationships

Generally, there were interesting features in the first melting of powders for pan blending where features were washed out and often displayed quite a different thermal behaviour on a second melting of the material once it had been crystallised from the melt. Sometimes unusual peaks occurred in this first melting which points to areas of incompatibility between the materials. The dissolution of powder grains in contact with other powder grains or a thin film of liquid was often influenced by the kinetics of dissolution. The polymer grains being bulk particles with dual amorphous and crystalline characteristics further complicated this dissolution.

Melting of all material combinations (after previously crystallising from the melt) appears to generally take the form of a classic, simple eutectic melt. Levels of polyamide below 20% have not been explored here and there is little data for blends at over 80% polyamide. Often a peak at the eutectic temperature is missing or faint at polyamide concentrations over 70%. In all cases there is a dip in the relationship between overall crystallinity (from the first DSC melting of ampoule samples) and polyamide concentration, meaning that there is negative enthalpy of mixing for blends.

It is also noteworthy that there seems to be a very approximate correlation across all material combinations that the greater the diluent crystallisation temperature is than the polyamide temperature, the higher the concentration where both materials crystallise together. This runs from near 0% for PA46PTh at $-111\text{ }^{\circ}\text{C}$ to 70-75% for PA6Car and PA612Car near $+45\text{ }^{\circ}\text{C}$ excess diluent crystallisation temperature. Results for PA69Car are indeterminate due to a paucity of results but appear to be greater than 64%.

11.3 Hydrogen bonding

The particular diluents had originally been chosen as potential model polyamide-polyamide hydrogen bond disruptors. The finding is that these

two hydrogen bond donors do not interact with the carbonyl acceptors in the polyamides.

Fourier Transform Infrared (FTIR) was carried out with sensitive photoacoustic spectroscopy in the mid range IR on all blend samples, leaving them in their original morphological state. Expectations from the literature on hydrogen bond complexation are that N-H peak values would shift by 15 to 30 cm^{-1} . “Free” N-H peaks, such as normally with the diluents, should shift to lower wavenumbers as the hydrogen bond interactions take place. Peaks for “bound” N-H should move to higher wavenumbers as the diluents form hydrogen bonds with carbonyl oxygen atoms, displacing the normal amide N-H to O bonds. The outcome should have been a move of the blend N-H peaks towards each other. In no blend sample was there a shift in peak frequency greater than 3 cm^{-1} . Often slight shifts seen with the peaks moving away from each other compared with simple summation of the spectra. This can be inspected for each material combination in the PDF files on the attached CD displaying actual spectra and the addition result from the spectra of the constituent materials.

Near Infrared experiments were carried out on all blends using the DRIFT technique in sensitive hydrogen bonding overtone regions. The peaks chosen were those close to the ones identified by Wu and Siesler [141] in their work on hydrogen bonding with polyamide-11. Spectra had been manually displaced vertically in Omnic software to check the match between the blend and its polyamide equivalent peak for each peak position. The original spectral overlays of NIR measurements on blends and constituent materials can be seen in the PDF files on CD. All peaks in the hydrogen bonding region of interest on all blend samples coincided exactly with the overtone peaks of the relevant polyamide.

The lack of N-H shifts for polyamide and diluent peaks in the Mid-range IR using the photoacoustic FTIR technique leads us to the conclusion that any interactions between the two materials on a molecular level do not involve hydrogen bonding between them. This was vindicated by using a different FTIR technique in the Near Infrared and finding that sensitive hydrogen bonding overtone bands of blends were unchanged from those of the raw materials treated in the same manner.

There is FTIR peak height information in the Mid-range IR band 1700 to 400 cm^{-1} that is ambiguous because of the non-linear response of photoacoustic measurements, making it difficult to assess whether there were actual differences in infrared absorption bands or not. Added to this was the observation of very bright pink colours in some samples and pink “freckles” visible under a binocularscope in pink hued samples. Together these could mean that pi-conjugation or charge transfer processes are taking place due to non-hydrogen bond interactions between the diluent and polyamide, perhaps with some phase separation. It is suggested that future researchers in this area may wish to pursue UV-visible spectroscopy and other techniques such as dielectric spectral analysis in addition to far more extensive NMR to investigate these aspects with a view to commercial applications.

11.4 Other areas of potential study for future workers

This work has covered a broad range of melting and crystallisation temperatures of the various material combinations and polyamide concentrations. The use of dynamic DSC crystallisation rather than isothermal crystallisation has been appropriate for the scale of the investigation. Other researchers may desire to look at specific material combinations using isothermal crystallisation because it is easier to treat the results from a theoretical perspective. The slow cooling experiments will have much in common, morphologically, with the “two step” isothermal crystallisation used by some authors [6, 160] because the crystallisations of the blend are staged. The fast cooling work here should approximate their “one step” crystallisations. The fast cooling here may, in fact, elucidate the order of crystallisation in their work in cases where the materials crystallise almost simultaneously.

Polyamide-6,6 had initially not been studied because the even-even polyamide-4,6 and polyamide-6,12 were already being studied and suitable samples uncontaminated with additives (fire retardant, processing, etc.) had not been located. Polyamide-6,6 has a melting temperature close to 260 $^{\circ}\text{C}$ which means that, based on the behaviour of the polyamides studied, crystallisation would be in the range 16-19 $^{\circ}\text{C}$ lower for cooling at 2 $^{\circ}\text{C}/\text{min}$ and 31-36 $^{\circ}\text{C}$ lower at 25 $^{\circ}\text{C}/\text{min}$. This puts its crystallisation temperature

approximately in the range 251-233 °C depending on cooling rate. These two values straddle the known crystallisation of carbazole at 237-233 °C at the same cooling rates. Experiments by other researchers with polyamide-6,6 and carbazole could use cooling rate to actively drive crystallisation into one morphology or the other. A lower molecular weight polyamide-6,6 could be used if the polyamide crystallisation temperature is too high or, alternatively, one of polyamides -4,8, -8,4 or -8,6 may be suitable, based on melting temperatures from Jones, Aitken and Hill [96].

The use of DSC as the only technique for investigating the morphology does have limitations because it is only “seeing” the crystalline portion of the sample. Temperature modulated DSC during cooling would be more appropriate for thorough investigation of glass transition temperatures of highly crystalline materials and for liquid-liquid demixing. Simultaneous Small Angle X-ray Scattering with Wide Angle X-ray Diffraction monitoring from the melt down to room temperature would allow investigations into the formation of the rich morphology that has been found. A further understanding of Brill transitions taking place and other crystallographic changes could also be studied at the same time.

11.5 Practical implications of the work

The most likely practical implications of the work are considered to be specialised membrane formation, drug delivery (and stability) and in melt processing for some specialised applications.

11.6 Summary of conclusions

The research in this project has led to increased understanding in areas of semicrystalline/crystalline binary polymer-diluent systems and the implications of relative melting temperatures of the components on the morphology of melt blends. It has given insight into the effects of polyamide repeat units (as distinct from melting temperature) on the behaviour the blends with carbazole or phenothiazine. It has also shown that any interactions there may be between the specific diluents and any of the four polyamides chosen do not involve the replacement of polyamide-polyamide hydrogen bonds with diluent-polyamide ones.