

## Chapter 2

### EXPERIMENTAL

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#### 2.1 Introduction

Many of the experimental details covered here are common to all combinations of the four polyamides with the two compounds melt blended with them. The eight major chapters covering the various

polyamide/compound combinations do not have experimental detail sections because everything is covered in this section.

## **2.2 Materials**

Polyamide-6 (Catalogue number 18,110,0), polyamide-6,9 (Catalogue number 18,806,9) and polyamide-6,12 (Catalogue number 18,114,5) were obtained as commercial grades from Sigma Aldrich. None of these grades were known to have any additives, which could potentially affect the blending process. These polyamides came as pellets approximately 3 mm in diameter and 3 mm long. The size was not amenable to many of the ways the polyamides were to be used. A coarse powder would be more useful. The granules were very tough, being polyamides. Various attempts using different methods were tried in order to make smaller particles. The most successful was to freeze the granules with liquid nitrogen and grind at high speed in a Breville CG-2 electric coffee & spice grinder having a flat metal blade. The coffee grinder had the lower inside casing of metal with a transparent polymer lid. A stainless steel plate was cut to just fit on top of the lower metal part in order to provide protection to the polymer lid. The fit of the plate was not perfect. This allowed the fine particles swirling around during grinding to slip through and settle on the metal plate. Automatic separation of coarse and fine powder from the larger particles and granule pieces being ground below was thus achieved. It was necessary to continually add small amounts of liquid nitrogen to keep the granules brittle.

Dr. Cor Koning (formerly) of DSM Research Laboratories was kind enough to provide 1 kg gratis of polyamide-4,6 having no additives. This material was provided as a coarse powder suitable for (near) direct use.

A range of potential hydrogen bond disruptors was obtained mainly from Sigma Aldrich. The two which were pursued in the main part of this research project were carbazole (Sigma Aldrich catalogue number C310,3) and phenothiazine (Sigma Aldrich catalogue number P1,483,1). These materials were provided in fine powder form.

## **2.3 Materials handling**

Polyamides are well known [99 p. 324] to absorb moisture into the amorphous portion of their bulk. The amount absorbed is 1-15%, depending upon the type of polyamide, level of crystallinity, temperature and relative

humidity [48 p. 358]. This moisture resides solely in the amorphous portions of samples. Moisture is unable to properly penetrate existing lamellae due to their tight interlinking by hydrogen bonding [122, 144, 145]. The moisture causes hydrogen bond disruption in the amorphous part, acting on either the carbonyl or N-H groups [48 p. 360]. Absorption into the amorphous portion can have very strong effects on the mechanical properties of polyamides, acting as a plasticiser [146, 147].

The above characteristic of polyamides was the reason that all samples were handled right through the various processes so that moisture ingress would be at a minimum. Materials were stored in a glovebox with low moisture content. The materials were weighed out in the glovebox. Any handling of raw materials or samples outside the glovebox was done in a way to minimise contact with (moist) air. Thermogravimetric Analysis (TGA) results on polyamide-6 in wet and dry states are presented in Chapter 4. It provides the necessary supporting evidence for the approach taken.

A Vacuum Atmospheres Company's Drilab double glovebox was available for storing materials and preparing samples. The glovebox was maintained at less than 7 ppm moisture during the whole of the period of this research. Initially it had been filled with Ultra High Purity argon gas (99.999% pure) from BOC but during the last two months of the project it was filled with High Purity nitrogen (99.99% pure) from the same supplier. This change is not considered to pose a threat to the validity of any of the experimental work carried out here.

The process, mentioned above, of creating powder from granules was carried out for convenience outside the glovebox. Polyamide powders were then dried under vacuum in the vacuum oven antechamber of the glovebox. The materials were placed in the vacuum oven in glass jars and held at close to 110 °C for a protracted period. The chamber was pumped down with an Edwards RV8 two-stage rotary vane pump until temperature and the vacuum level were achieved and then the vacuum pump turned off after the valve to the chamber was closed. This meant that there was no backstreaming of oil vapours from the pump into the vacuum oven chamber and onto the samples being vacuum-dried. Backstreaming could otherwise have occurred during the extended time the powders were being dried. The

heater was controlled at the required temperature. Cooling water was passed through the chamber walls and door to keep them cool. This had the effect of capturing any moisture released from the material being dried. A pressure of approximately 150 Pa was maintained during the drying process. Vacuum drying was initially carried out for 96 hours. That was dropped to 16 hours in later polyamide drying after discussions held in April 1999 with Dr. R. Gaymans of Twente University in the Netherlands. Vacuum dried materials were transferred directly inside the glovebox from the vacuum oven antechamber. The materials were stored in the glovebox until required. Caps of the jars were left loose to allow equilibration with the glovebox interior.

Polyamide-4,6 powder from DSM was opened in the glovebox. The material was vacuum dried in the same manner as the other polyamides so that a consistent environment was common for all polyamides. The dried polyamide-4,6 powder was stored afterwards in the glovebox.

Seals of all potential hydrogen bond disruptors were opened in the glovebox and the material containers left open for a week with a cover approximately 1 cm above the rim to allow moisture stabilisation and reduce potential ingress of any dust.

An AND model HA-180M balance was available within the glovebox for weighing materials. It was generally stable to approximately 0.2 mg but at times drifted by several milligrams over a short period. It was found best to allow it to stabilise for at least several hours when the balance started drifting substantially.

An hermetic pan crimp was available within the glovebox. Pans and lids for the DSC were weighed on a Cahn microbalance Model C-34 outside the glovebox before being brought into the glovebox. The Cahn instrument gave reproducible measurements to within 10  $\mu\text{g}$ . The mass was marked with a fine permanent ink marker on a stoppered glass vial container used for transport of the pan. Materials were added in the glovebox with the less sensitive AND balance there, giving approximately the desired amount. Extra care was taken for the cases where more than one material was being added to a pan. The balance was checked for zero before and after measurements to ensure that drift had not occurred. Measurements were

repeated until stable results could be obtained. Pans were crimped in the glovebox and reweighed later on the more accurate Cahn microbalance. The weight of the sample prior to DSC was also marked on the vial.

TGA samples of 10 to 15 mg were weighed on the AND balance. Sidecutters were used to cut TGA samples from larger pieces. Tweezers were used for handling the small pieces involved. A scalpel was not used for cutting small pieces because of a risk of damage to gloves and injury to the operator. The sidecutters also had the advantage that they tended to contain the small pieces when cutting hard materials. Pieces for TGA were stored in vials with tops and the vials marked with the origin of the sample. These samples in airtight vials could safely be stored outside the glovebox until ready for use because the gas inside was dry from the glovebox environment.

## **2.4 Preparation of Melt Blends**

There are two basic ways to make blends, from solution or from the melt. There were initial attempts to create complexes from solution. This had been on the advice that melt complexing would be difficult due to problems in finding suitable materials where evaporation or degradation were not serious issues at the working temperatures involved for melt blending. The solution work was not successful in creating complexes. That work is not covered in the thesis.

The melt blending proceeded firstly with experiments in DSC pans to evaluate the possibilities on a small scale and then to larger scale experiments in glass ampoules once the small-scale work looked promising.

### **2.4.1 Melt Blending in DSC Pans**

Initial work utilised the temperature controlling facilities of a DSC in order to carry out melt blending. The advantage was the ability to thermally monitor potential complexation with DSC during the actual melt blending process. There was a disadvantage in the small amount of blended material being produced (approximately 0.01 g).

The hermetic pans were accurately weighed prior to introduction into the glovebox. As close as possible to 5 mg of the relevant vacuum dried polyamide powder was weighed into the pan using the balance in the glovebox. Either 1, 3, 5 or 8 mg of the potential hydrogen bond disruptor was added on top of the polyamide. The pan was crimped hermetically in

the glovebox using the appropriate closure tool. The pan was then weighed accurately again outside the glovebox using the more accurate balance outside.

Melt blending in the DSC was initially carried out at 5 °C/min heating rate followed, after 7 min in the molten state, by crystallisation at 25 °C/min. This was done for some of the blend ratios mentioned above and also for the individual starting materials as a reference.

Some DSC runs were also carried out for a cooling rate of 2 °C/min instead of 25 °C/min in order to give the molten mixture more time to form crystals. This was under the more adverse conditions of having the diluent evaporating from the “hermetic” pan for longer periods at elevated temperatures. This was not carried out extensively because the project had already moved from blending in pans to making greater amounts of material at the same time in ampoules.

The disadvantages of carrying out the process in the DSC are that the amount that is produced by this method (6 to 13 mg) is far too small for most analysis techniques such as Fourier Transform Infrared spectroscopy, Nuclear Magnetic Resonance spectroscopy and Small Angle X-ray Scattering. There is also a problem in that the different analysis techniques use differently configured samples in terms of particle size and form. To avoid these difficulties, blends of larger size were made in ampoules.

#### **2.4.2 Melt Blending in Ampoules**

The ampoules used were made from thick walled glass tubing 16 mm Outer Diameter (OD), 2.5 mm wall thickness and sealed at one end. They were 250 to 300 mm long with the middle 80 to 100 mm necked down to approx 3 to 4 mm Internal Diameter at the narrowest.

The polyamides used had very low percentages of moisture because raw materials were kept in a glovebox with either dry argon or nitrogen. This meant that the polyamide tended to become electrostatically charged and stick to the walls of the glass ampoules. A solution was found to the problem of filling ampoules by first putting the diluent in the ampoule. That left a very fine layer of powder on the glass. The polyamide powder being added later would slip easily through to the bottom section and not cause problems in adhesion to the glass walls.

The required quantities of diluent and polyamide were weighed out into containers using the AND balance in the glovebox. The materials could then be fed into the top section of the ampoule to make the blending charge. The vast majority of powders adhering to the inner walls of the top section could later be scraped down through to the neck section using a thin spatula with a bent, rounded end. There was usually a very small amount of material adhering to the inner walls of the top and neck sections. This would have not substantially altered the ratios of materials in the charge, as that was relatively large at 1.5 g. A suitable polyethylene vial stopper was fitted to the top to seal against moisture ingress when the ampoule assembly was later removed from the dry glovebox.

Sealing the ampoule neck was done outside the glovebox. The stopper was quickly removed and a vacuum hose attached to the top opening. The hose led, via a liquid nitrogen cold trap, to a rotary vane vacuum pump. The ampoule was evacuated for at least 10 minutes despite the small volume of the ampoule. That was because the small neck in the ampoule would restrict achieving a good vacuum within the volume where the charge was situated. The bottom section of the ampoule (containing the charge) was lowered into a thermos flask filled to the very top with liquid nitrogen. The charge was held at least 20 mm below the liquid nitrogen surface by a clamp so that glass above the charge was at liquid nitrogen temperatures. That meant the ampoule sealing operation would not degrade the charge materials. A large natural gas/compressed air Bunsen burner was then used to heat the ampoule neck whilst the system was still attached to the vacuum system. The glass eventually softened sufficiently for the neck to collapse under the vacuum. The ampoule body with charge could then be sealed off and removed. The materials in the charge were then manually shaken and turned over for five minutes to mix them thoroughly after the ampoule body had returned to room temperature.

A custom-made furnace, manufactured by Scientific Equipment Manufacturers, and capable of over 1000 °C was available for the trials. The furnace cavity was 150 mm wide, 270 mm deep and 90 mm high. There was a thermocouple controlled BTC-8080 PID controller with the capability of heating at a predetermined rate to a predetermined temperature. There was

also a separate sensor with power cut-out for thermal runaway events and an exhaust vent. The controller could not be set to cool apart from manually being set to lower temperatures in a stepwise manner.

The first ampoule (see Chapter 3) was essentially carried out as a “dry run” to determine where all the problems with blending in ampoules would lie. The ampoule was mounted in a metal tube (against a possible explosion) in a nearly horizontal position supported above the furnace floor. That ampoule had overshoot the 300 °C set temperature and had gone to 320 °C due to thermal inertia in the system. The temperature setpoint was quickly lowered manually to 280 °C and set 20 °C lower every 10 minutes. The furnace had dropped quickly in the initial cooling stages but soon lagged well behind the regular manual drops in setpoint. The outcome with this ampoule was the solid being coloured quite differently in three sections along its length, as described and shown in Chapter 3. Attempts over the next seven ampoules to repeat the separation into differently coloured sections of differing compositions were unsuccessful. The alternative strategy was to make the materials deliberately with the desired compositions in a very controlled manner. The first step was to ensure that the ampoule was exactly horizontal so that both ends would cool at the same rate.

Thermal control over the process also had to be improved. This led to replacing the controller with a 7-step Temptron controller that could be programmed with FCLink software. The software was run on a laptop computer connected to the controller with an RS-232C serial connection. The controller chosen had the possibility of switching an alarm function on or off for each programmable step. That possibility allowed the alarm signal to be connected to a solenoid. Compressed air was run to the furnace via the solenoid and introduced to the furnace cavity via a metal pipe placed in the exhaust vent. The air entered one side of the furnace and circumvented a baffle. Air left on the other side via the exhaust vent after passing the ampoule. The compressed air could work against the heater to provide better heating and cooling control. The maximum temperature during furnace runs was 300 °C and the furnace was designed for quick heating to over 1000 °C so forced air cooling at 2 °C/min was not considered deleterious to the ceramic furnace interior. Constant cooling at 2 °C/min

with the compressed air could be maintained down to less than 100 °C although it was usually only continued at that rate to 140 °C in order to shorten blending runs. Crystallisation activity was normally completed by 140 °C. The existing encased thermocouple was replaced with a thin wire one placed close to the ampoule to ensure that the controlled temperature represented the temperature of the material in the ampoule as closely as possible. The use of a closed, thick metal tube to protect people from potentially exploding ampoules was also not in the interests of good thermal responsiveness and control. The use of the tube was dropped after the first few ampoules were produced, as the risk of damage to the ceramic furnace liner appeared low and better thermal control could ensue. Instead, a lock and a notice were put on the door opening mechanism of the furnace during the melt blending process. It can be noted that none of the ampoules broke in the furnace although the potential for breakage or explosion still existed.

The profiles used normally with the furnace were to heat the ampoules at 5 °C/min, hold the temperature at 260 °C for 1 hr before a sharp excursion to 325 °C in the melt for 5 min and cooling at 2 °C/min. Initial ampoules were varied and carried out with various profile variants and manual cooling. Results presented in the various chapters (with the exception of Ampoule 1 in Chapter 3) are from later ampoules using the temperature controller and forced-air cooling. Profiles were varied in the very early trials to achieve the most consistent composition throughout the sample as determined by Thermogravimetric Analysis (TGA).

The results of the first ampoules had showed that having a circular cross section to the ampoule made the bulk material harder to present samples for FTIR and other techniques. The cooling of the material would also have been uneven, with the middle part of the cross-section thicker and therefore cooling at a different rate. It was better to have a relatively thin bulk sample of even thickness and spread out over a larger area if consistent material were to be formed. This led to most of the material coming from the trials being made with ampoules having one side flattened during manufacture. The outcome with an accurately horizontal ampoule in the furnace was a piece of near rectangular bulk sample with a nearly consistent 2 to 3 mm thickness from 1.5 g of constituent materials.

The ampoules from melt blending had a vacuum inside when back at room temperature because of the original sealing process. An inrush of moist air at opening would most likely cause adsorption of moisture that would later be absorbed into the material. Opening the ampoules could not be done in the glovebox because of the difficulty in breaking the ampoules open. Opening was carried out in a plastic bucket filled with cold dry nitrogen and covered with a sheet of plastic. The nitrogen was from liquid nitrogen in the bottom of the bucket. The ampoule had previously been scored around the middle with the edge of a triangular file. The ampoule was held under cover in the bucket with rubber gloves on as protection from glass splinters/shards. It was hit with a hammer to break the glass and the pieces of blend material placed immediately in a jar that was quickly closed.

Jars were put as quickly as possible in the glovebox via the antechamber and opened inside to the dry atmosphere. Material was stored in stoppered vials in the glovebox after a stabilisation period of several days. The pieces of material from the various trials could be kept permanently in the glovebox until cut up with sidecutters for the various trials.

## **2.5 Thermogravimetric Analysis**

Thermogravimetric Analysis (TGA) to determine the polyamide weight percentage in ampoule samples was carried out with a TA Instruments Hi-Res Modulated TGA model 2950 Thermogravimetric Analyser. Experimental work was carried out over an extended period and several upgrades of the Instrument Control software were made during that period. Software changes were unlikely to have affected the experimental outcomes.

Samples of material from the ampoules were cut to 10 to 15 mg total weight in the dry glovebox where the ampoule material was stored. Pieces were placed in small, stoppered glass vials marked with the contents. Some samples were crumbly and some were difficult to cut to near the desired weight range because they were so hard. Attempts were made to have the TGA samples in one (or two) pieces but that was not always possible. TGA samples were taken from bulk ampoule material next to where DSC samples were removed so that the effects of any composition variations in the bulk sample would be minimised. An AND model HR-180 balance in the glovebox was used for weighing samples to better than 1 mg accuracy. The vials were

removed from the glovebox and TGA was carried out within 24 hours to avoid any potential moisture leak past the seal on the plastic top.

The TGA stirrup with an open Standard DSC Aluminium pan was tared just prior to the experiment. The vial was opened minutes before TGA was carried out, the sample placed in the DSC pan on the stirrup (on the loading table) and the experiment run. The DSC pan was used to minimise contamination of the stirrup. The purge gas was High Purity nitrogen (99.99%) from BOC Gases used at a flow rate of 50 ml/min in both gas streams. TGA was run from room temperature to 500 °C at 10 °C/min. Initially all measurements were carried out in High Resolution mode with settings Resolution = 4 and Sensitivity = 4. Later in the series of experiments, duplicate samples were taken so that TGA could also be carried out ramping straight through from approximately 25 to 500 °C at a fixed 10 °C/min. The two samples were taken from either side of where DSC samples were removed from the bulk Ampoule material. The High Resolution runs are identified as “R4S4” and the others as “Straight” in the text.

Generally, phenothiazine and carbazole material started evaporating at 175-200 °C in a TGA instrument. The weight remaining reached a plateau before 275 °C as the carbazole or phenothiazine evaporated from the sample. Degradation of the polyamide began above 325 °C at the ramp rates involved. The weight percentage remaining at 300 °C was taken as the percentage of polyamide in the sample.

## **2.6 Differential Scanning Calorimetry**

Differential Scanning calorimetry (DSC) was carried out on a TA Instruments DSC 2920 Modulated DSC instrument with their Instrument Control software running on a PC.

### **2.6.1 Calibration materials and their preparation**

Pure indium wire for Cell Constant and Temperature calibration was obtained from TA Instruments. 10.515 mg of indium wire was then weighed into an aluminium hermetic DSC pan as supplied by TA Instruments.

Fine Al<sub>2</sub>O<sub>3</sub> powder from TA Instruments was dried by holding it in a furnace at 600 °C for 30 min under an oxygen atmosphere. Approximately 6 mg of this Al<sub>2</sub>O<sub>3</sub> powder was quickly placed in an hermetic DSC pan and the lid

crimped. The powder was lightly pressed by the lid to the bottom of the pan for good thermal contact.

### **2.6.2 Calibration**

Calibrations were run before every series of experimental runs. A baseline was run at the same ramp rate as experiments were to be run (5 °C/min) over the range 25 to 320 °C. Cell Constants were calibrated at 5 °C/min using indium with its known heat of fusion 28.45 J/g [128 p. 144] . This calibration ensures the correct enthalpy value when integrating peaks in thermograms of samples. The very sharp melting peak of indium was also used to calibrate temperature. Experiments were run using Temperature Modulated DSC so that “Reversing” and “Non-reversing” signals could also be extracted if needed. Calibration of the Heat Capacity Constant for the experiments was done using dried Al<sub>2</sub>O<sub>3</sub> as a calibrant. The range of interest was from 100 to 300 °C. The calibration coefficient varies by 5% even over the very limited range 170-250 °C. Calibration was done under the same conditions as those used for experiments, viz 5 °C/min average ramp rate with a period of 30 s and amplitude of 0.41 °C. The short cyclic period was necessary because some transitions had been found to occur sharply and there should be four cycles over a transition [129 p. C-32, 148] to avoid artefacts in the thermograms. The amplitude was the maximum that kept a heating ramp from temporarily becoming cooling during a portion of each cycle. The maximum amplitude was chosen in order to enhance sensitivity for extraction of the “Reversing” signal. Helium gas was chosen for the purge gas because nitrogen has too slow a heat transfer to the pans. See Appendix B for a discussion of the approach taken to TMDSC. The flow rate in both gas streams was 50 ml/min.

There was no opportunity within the TA Instruments DSC Instrument Control software used to change calibration settings during the actual course of the runs. The cooling parts of the runs were therefore done without using temperature modulation as it is recognised that the cooling parts are not calibrated properly. That applies, in general, where TMDSC work is carried out with different heating and cooling rates.

Cooling from the melt was at 25 °C/min for early experimental runs. Experiments testing the instrument “process capability” showed that

25 °C/min was the fastest cooling rate that could be maintained under proper instrument control over the temperature range of interest. That required the heater switch on the Liquid Nitrogen Cooling Accessory (LNCA) to be in position 3.

The experiments with the DSC using ampoule material and some with melt blends in pans were carried out incorporating cooling at 2 °C/min to give more opportunity for slow crystallisation to take place whilst retaining practical times for experimental runs.

### **2.6.3 Experimental trials**

DSC runs were carried out in hermetic pans with sample masses in the range 7 to 15 mg (and predominantly between 8 and 10 mg). This is taking into consideration TA Instruments' recommendations of 5 to 10 mg for DSC investigations of melting/crystallisation temperatures and crystallinity [129 p. 3-12], that their recommendations for TMDSC with polymers are 10 to 15 mg [129 p. C-74] and that we have two materials in the sample being heated and cooled through their transitions. The larger sample weights tended to be used where there was a smaller percentage of polyamide in order to keep the polyamide transition signals at a reasonable level. Hermetic pans can ideally contain pressures up to 4 Bar. Some loss in weight was experienced in each heating/cooling cycle. The loss was most likely due to the hermetic pans being less than perfectly sealed. It was not due to the degradation of the polyamide or loss of any very slight residual moisture as the loss was not experienced with pure polyamide samples. Carbazole has a melting temperature of 246 °C and a boiling temperature of 355 °C. There would be a reasonable vapour pressure at 300 °C. Any loss of vapour diffusing out of an imperfectly sealed pan (and removed in the helium gas stream) would be replaced from the solid diluent in the pan in order to maintain the equilibrium vapour pressure for that temperature. This would result in a continuous loss of carbazole whenever the vapour pressure was high and the pan not perfectly sealed. Obviously a higher temperature and longer period at the high temperature will lead to a greater the loss of carbazole from the "hermetic" pan. Similar comments apply to phenothiazine.

Polyamide-4,6 melts at 290-300 °C but it degrades if left at temperatures over 300 °C for extended periods. The degradation can be seen afterwards by slight yellowing. The polyamide will also experience an increase in molecular weight if left for long periods near the melting temperature [48 p. 307]. The period in the melt had to be long enough to melt all the lamellae but these restraints on extended periods at high temperatures meant that there was little flexibility with temperatures and times. Polyamide-4,6 thus had a narrow processing window for the trials.

The procedure was to ramp the sample from 25 °C to 307 °C at 5 °C/min. The sample was held at the set maximum temperature for 5 min in order to allow the sample to melt properly. Cooling took place at 25 °C/min or 2 °C/min rate to 25 °C. This cycle was repeated within the trial run after a 7 min delay at 25 °C. Usually the actual temperature was approx. 3 °C behind the setpoint when the heating ramp finished. The sample then stabilised rapidly at the set maximum over the holding period. The temperature profile used for polyamide-4,6/phenothiazine was the same one despite the much lower melting temperature for phenothiazine because the polyamide-4,6 still had to be fully melted.

Ramp profiles were similar for polyamide-6, polyamide-6,9 and polyamide-6,12 with the difference that the maximum temperature was set at 260 °C. That ensured all carbazole in polyamide/carbazole trials was melted. Polyamide/phenothiazine trials were carried out using the same profiles for consistency in approach.

### 2.6.3.1 Melt Blending in Pans

The blending process of heating the dried powders at 5 °C/min (modulated as above) until they had both melted and the crystallisation at 25 °C/min could be monitored *in situ*. This was followed by a repeat run on the blended material to monitor how the melt-formed material performed thermally after solidification had been completed in the ampoule.

### 2.6.3.2 Melt Blending in Ampoules

No thermal monitoring of the blending process could be performed directly where it took place in an ampoule. This means that the first run on material from an ampoule is equivalent to the second run with blending in DSC pans. A repeat monitoring run was additionally performed on the material from

ampoules. These were all carried out with a heating rate of 5 °C/min (modulated as above) and cooling at 2 °C/min.

### **2.6.3.3 Additional trials covered in Appendix B**

The results referred to in Appendix B differed from the main part of the thesis in that they were carried out early in the project with Temperature Modulated Differential Scanning Calorimetry (TMDSC) at a ramp rate of 2 °C/min with amplitude of 0.212 °C and a period of 40 s. This results in a minimum heating rate of zero during each cycle. Further detail on the choice of TMDSC conditions for that work is covered in the appendix, along with other information pertinent to TMDSC experiments.

Baseline, Cell Constant, Temperature and Heat Capacity Constant calibrations were carried out prior to this work under the same conditions. The work in the appendix explored the effects in the case of Al<sub>2</sub>O<sub>3</sub> of helium versus nitrogen as the purge gas and of reducing the helium flow rate. Lissajous figures are used to evaluate thermal delays in the equipment and these are described in the appendix.

There is also a trial melting polyamide-4,6 carried out with TMDSC under the same ramp and cycle conditions as the Al<sub>2</sub>O<sub>3</sub> and using helium at 50 ml/min as purge gas. Sample material and preparation for this work was identical to that for the main part of the thesis.

## **2.6.4 DSC Thermogram evaluation**

### **2.6.4.1 Melting and Crystallisation temperatures**

Melting and crystallisation temperatures reported in the text are taken as the peak temperatures unless otherwise noted.

### **2.6.4.2 Enthalpies from Graphical Analysis**

Melting and crystallisation enthalpies were measured using the “Integrate Peak” capabilities of TA Instruments' Universal Analysis program. The Sigmoidal Tangential option was consistently used in Enthalpy of Fusion ( $\Delta H_f$ ) determinations because sometimes the two sides of a peak were not exactly parallel. Occasionally, two peaks partly overlapped. The double peak was integrated using the “Sigmoidal Tangential” option and then a “Perpendicular Drop” was placed to separate the two areas. The placement of the Drop was positioned so that the estimated tail from one curve was equal in area to the estimated tail from the other. One peak was sometimes

a shoulder on another other peak. It was more difficult to accurately estimate the appropriate areas attributable to each. Usually it was possible to make estimates based on different premises. These were then averaged to give the best estimate. There was occasionally a ‘spiky’ crystallisation of carbazole or phenothiazine part way through another crystallisation with a Gaussian form. The leading edge of the carbazole/phenothiazine crystallisation was non-Gaussian. The most appropriate way of tackling that was to take the “Sigmoidal Tangential” integral over the double peak and to subtract the “Linear Integral” over the carbazole or phenothiazine peak from it to give the integral over the Gaussian peak.

#### 2.6.4.3 *Crystallinity calculations*

Total crystallinity determination was made by comparing the measured total enthalpy from melting with that expected on a weight proportional basis from literature values for 100% crystallinity of the polyamide and the diluent.

The weight percentages for samples blended in pans were taken from the weights of the constituent powders. For the ampoule samples, these were taken from the high resolution TGA “R4S4” results from samples taken next to the DSC samples.

## **2.7 Simultaneous Differential Thermal Analysis-Thermogravimetric Analysis**

The equipment used for Simultaneous Differential Thermal Analysis – Thermogravimetric Analysis (SDT) was a TA Instruments Model 2960. The furnace with an SDT instrument is horizontal as distinct from the vertical furnace of a TGA instrument. This means that the gas flow around a sample will be different from the TGA and different again to the DSC. DSC has the sample in a closed pan. SDT does provide a means of quickly comparing various materials.

Trials were run with nitrogen at 50 ml/min. Heating ramps were carried out at 10 °C/min.

## 2.8 Fourier Transform Infrared Spectroscopy

### 2.8.1 Mid Infrared Range Measurements

Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy was initially carried out on a Nicolet Magna Spectrometer Model 750 with DRIFT attachment. A few samples from Ampoule 1 (PA46Car), carbazole powder and polyamide-4,6 powder were tried. This led to some inconclusive results with possible frequency shifts when comparing the resulting spectra of the blends to those of the starting materials. It was suggested that the narrower peaks associated with Photoacoustic spectroscopy (PAS) could alleviate the problems. Consequently, the results presented in the text for Mid Range IR were carried out on the Nicolet 750 but with an MTEC model 300 PAS attachment. This was operated in the frequency range 4000 to 400  $\text{cm}^{-1}$  at a resolution of 8  $\text{cm}^{-1}$  with an IR source, KBr beamsplitter, a mirror velocity of 0.1581  $\text{cm/s}$  and an aperture setting of 130. Ultra High Purity (99.999%) helium gas from BOC was used at a flow rate of 20  $\text{ml/min}$ .

Background calibration prior to the measurements on blends was with 512 scans of a carbon black standard from MTEC. Trials showed that it was necessary to re-calibrate every 4 to 5 hours. The entry of the carbon black sample holder in the PAS attachment and flushing took place at a much slower rate than the manufacturers' recommendations on the advice of a colleague [149] who had had extensive PAS experience. The first stage of flushing was held for 10 minutes, and the later ones for two minutes before complete closure took place and measurements began. There was usually little evidence of  $\text{H}_2\text{O}$  peaks in the background spectra. Background calibration was repeated, if necessary, until satisfactory elimination of moisture peaks was achieved.

Samples of approximately 7x7x2 mm were cut in the glovebox from the material extracted from the ampoule and then placed (with dry atmosphere) in small glass vials with airtight stoppers. The samples could then be kept completely dry until they were put in the photoacoustic holder. This was in order to minimise the potential effects of moisture ingress. Samples were fitted to the PAS holder and placed immediately in the dry helium environment of the photoacoustic detector. The pieces of material from the various ampoules were usually placed bottom side (from the ampoule)

upwards in the sample holder as this surface was flat. They had to be fitted in several pieces to the holder in some cases where the material had been too crumbly to use a single piece. The samples were set at approximately 1 to 1.5 mm under the lip of the holder using shims under the sample. This height gave the best results and was in line with the manufacturer's recommendations [150 p. 6]. Signal levels were checked prior to each trial run to ensure that they were not so low that noisy results ensued and that there was no risk of saturation of the detector amplifier. The first stage was held for 5 minutes and the later ones for a minute before complete closure took place. Samples were run for at least 256 scans.

### **2.8.2 Near Infrared Range**

It is specifically in the Near Infrared (NIR) range 6900 to 6100  $\text{cm}^{-1}$  and 5000 to 4500  $\text{cm}^{-1}$  that hydrogen bonding effects are to be expected [141]. Measurements were carried out on the same Nicolet 750 instrument as for the mid-range experiments but with a white light source, a  $\text{CaF}_2$  beamsplitter and a PbSe detector. That configuration for NIR experiments covered the range 11,000 to 2100  $\text{cm}^{-1}$ . The changeover was easy to make but required 24 hours stabilisation of the system before measurements could be made because the whole instrument had to be opened to the atmosphere during the changeover process. The best results were obtained with the sample in a Diffuse Reflectance Infrared Fourier Transform (DRIFT) attachment rather than the PAS attachment. A sample size of approximately 7x7x2 mm was used, as with the mid-range experiments. The sample height needed to be adjusted for each sample to give the maximum signal, or the signal/noise ratio was poor. A stabilising period prior to measurement of approximately 20 min was necessary to eliminate moisture from the measurement chamber after having opened it for sample insertion and height adjustment. Background and sample runs were at least 256 scans at a resolution of 4  $\text{cm}^{-1}$  and a mirror velocity of 0.9494  $\text{cm/s}$ . Background calibration was with dry KBr. The spectra for the ampoule material from blends could be directly compared with those from ampoules of the constituent materials without the modelling used in the Mid Range because of the broader peaks involved.

## 2.9 Small Angle X-ray Scattering

Mr Clint Gamlin of the Ian Wark Research Institute at the University of South Australia spent some time in late 2000 at the University of Connecticut, USA carrying out Small Angle X-ray Scattering (SAXS) for his own project. He was kind enough to run some of the samples available from ampoules whilst there. The samples were sent sealed against moisture to Connecticut.

The equipment had been custom built in the University of Connecticut. Conditions used were 627 ±5 mm sample to detector distance. A 40 kV 100 mA Cu source was used. The main wavelength is 0.154 nm. Scattered X-Rays co-operatively interfering from reflection planes in the sample were collected using a 2-D area detector.

Material was pulverised in a mortar and pestle and then contained between Kapton films. Vacuum was achieved with a rotary oil pump for 5 min (approximately 0.150 Pa) before measurement runs having a duration of 1 hr. A blank run was made with the Kapton film but no sample. There was little scattering from the Kapton film. No peaks were evident at the angles used. Results were obtained after determining the centre of the circle by changing the radius and centre of an overlaid circle. The spectrum was then determined by integrating around the signal circle. Custom software was used for this. These results were saved as a tab delimited text file. Making a running average over three points smoothed the raw results and did not affect accuracy as peaks were broad. The background scatter results were subtracted from the measured values to give corrected smoothed curves.

## 2.10 Cross Polarised/Magic Angle Spinning Solid State <sup>13</sup>C Nuclear Magnetic Resonance Spectroscopy

All spectra were run on a Bruker MSL300 operating at 300.13 MHz for <sup>1</sup>H and 75.482 MHz for <sup>13</sup>C. Experiments were performed with a standard Bruker 4 mm Magic Angle Spinning (MAS) probe. The MAS spinning speed was approx. 5 kHz. The 90° pulse times for both <sup>1</sup>H and <sup>13</sup>C were 4.1 μs. The spectra were recorded using the standard cross polarisation sequence with a 3 s recycle delay and high power proton decoupling during acquisition. The cross-polarisation contact time was 1 ms. The spectrum width was 38.5 kHz, and 2000 data points were collected. Single pulse

excitation spectra were collected under the same conditions and with a recycle delay of 3 s. On processing, a line broadening of 50 Hz was used, and the files were zero-filled to 4k data points. Chemical shifts are referenced to TMS via the external standard adamantane.