Research Article

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Crystallization and dissolution behaviour of polyamide 6–water systems under pressure

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Abstract

The solubility of polyamide 6 (PA6) in water under pressure has been reported recently and is explored further here using a pressurized differential scanning calorimeter equipped with a pressure regulator, enabling operation at constant pressure. The optimum parameters for solubility (temperature, pressure, concentration) were determined. Crystallization and melting temperature depressions of a maximum of 60 °C were found. The minimum water concentration needed to reach the maximum temperature depression was found to be approximately 30 mass%. Because in such a case the end melting/dissolution temperature for PA6 in water is approximately 165 °C, the pressure level has to be high enough to prevent water from evaporating, i.e. above 8 bar (0.8 MPa). The expected industrial uses of the water solubility of polyamides under pressure are to ease the processing of polyamides by extrusion; to make polyamide composites; to disperse temperature-sensitive fillers in polyamides; and, in general, to realize 'green' routes for the formation of polyamides.

Keywords: temperature depression; high-pressure differential scanning calorimetry; energy saving; polyamide

INTRODUCTION

Recent work carried out on polyamide 6 (PA6) and polyamide 4.6 (PA4.6) has highlighted the fact that these polymers are fully soluble in water at elevated temperatures under pressure[1–3] and that the addition of water in general decreases notably the melting and crystallization temperatures of polyamides, while, for kinetic reasons, hydrolysis remains limited. The start of this research was based an a concept developed at DSM Research in the early 1990,[4] and was applied[5] to dissolve polyamides (PA6, PA6.6, PA4.6, etc.) in water and other solvents (such as methanol, butanol and ethanol and mixtures thereof) at elevated temperatures under pressure, work which has triggered research by other groups since then.[6]

These researches are of great interest concerning the processing of polyamides as well as the compatibilization of hydrophilic fillers with polymeric resins.[7] However, the standard DSC technique used involves pressure-resistant stainless DSC pans, leading to a high percentage of leakages with corresponding risks for the device. Moreover, in such a system, pressure and temperature are linked.

In the study reported here, an attempt was made to determine the parameters required to obtain solubility and to observe the cryoscopic effect. For that purpose, a pressurized differential scanning calorimeter was used, allowing the regulation of temperature and pressure independently. Initially, water was tested in order to validate the device and the protocol. Then, virgin PA6 was studied in order to determine its melting and crystallization behaviour. Lastly, water and PA6 were mixed under various pressures and at various water concentrations in order to determine the optimum parameters to realize maximum lowering of the melting and crystallization temperatures of PA6.

MATERIALS AND METHODS

The PA6 used was provided by BASF (Ultramid B27E). The original pellets (which weighed *ca* 12 mg each) were transformed into powder (of 1 mm in size and less than 1 mg) using a Fritsch Pulverisette. The water concentration of this powder as produced was determined using TGA and was found to be about 2.5%. In this study, the PA6 was never dried before being tested; 'pure' PA6 means here 'not dried' and 'without added water'. According to the literature, the melting point of PA6 ranges between 220 and 225 °C.[1,8–10] Demineralized water was used to dissolve the PA6 under pressure. Measurements were carried out using a Mettler Toledo HP-DSC (Fig. 1) equipped with a pressure regulator (accuracy of ±0.1 bar (±10 kPa)). The pressure, built up using nitrogen gas, could be set between 1 and 80 bar (0.1 and 8 MPa). The temperature and energy calibration was performed at a heating rate of 10 °C min^{-1} under a pressure of 1 bar (0.1 MPa) of nitrogen using indium and zinc.

The protocol used to characterize water, PA6 or PA6–water was as follows. A defined amount of water (measured with an accurate pipette) was put in a 40 µL aluminium crucible (beforehand put in a flame to prevent the material oxidizing). The required amount of PA6 powder was separately weighed and added to the water in the crucible. The amounts of water and/or PA6 were chosen so that the tested sample generally weighed *ca* 15 mg. A tapped lid with a 50 µm hole was fixed onto the crucible and an empty reference crucible was prepared with the same materials. The two crucibles

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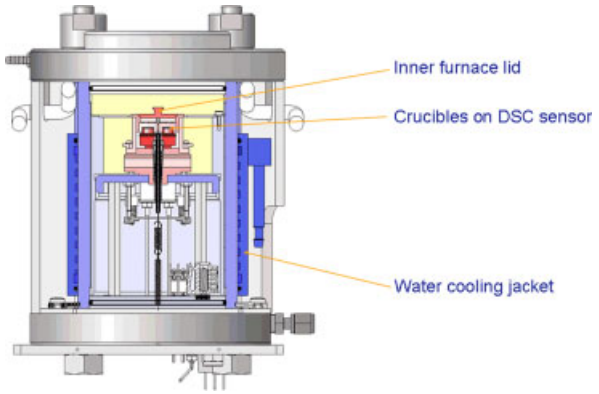


Figure 1. Schematic representation of the high-pressure DSC apparatus.

were then positioned, the system closed and the pressure set to the desired value.

Various temperature–time ramps were defined, mainly by varying the scan rate. As a standard procedure, the combination of a cooling rate of 10 °C min^{-1} and a subsequent heating rate of 10 °C min^{-1} was chosen. Two stages of temperature stabilization (at 200 °C for 10 min and at 60 °C for 5 min) were added to the cycle in order to allow the mixing of water and PA6.[1] To determine the boiling point of water under various pressures (from 1 to 80 bar (0.1 to 8 MPa)), a heating rate of 10 °C min^{-1} was applied to the cell from 25 to 300 °C. Also, other scan rates (5, 20 or 40 °C min^{-1}) were used to investigate the effect of various parameters on the melting and crystallization temperatures of pure PA6.

In the following, DSC curves are plotted upwards in the case of heating and downwards in the case of cooling. The first heating curve is not considered as it depends on the (unknown) thermal history of the sample. The peak temperatures were determined for each specific phenomenon (crystallization and melting), because they best reflect the thermal behaviour of polymers. Finally, each experiment was performed at least three times to check repeatability.

RESULTS

Validation of the pressure device

The experimental values obtained for the boiling onset temperature of demineralized water under pressure (Fig. 2(a)) are close enough to the data found in the literature (Fig. 2(b)). This validates the pressure device and the methods used.

Experiments carried out on pure PA6

Influence of sample morphology

Testing of both PA6 pellets and PA6 powder shows that lowering the pellet sample mass (from 12 to 0.3 mg) lowers the melting peak temperature (from *ca* 226 to *ca* 222 °C). This reflects decreasing temperature gradients within the pellet leading to a reduced thermal lag. For powder samples, the sample mass is much less critical because the powder spreads much better on the bottom of the sample pan. Thermal gradients are thus negligible under the conditions used as is the resulting thermal lag. In addition, because the dissolution of PA6 powder will be optimal because of its high surface area, this sample morphology was adopted for further experiments.

Influence of heating and cooling rates

For pure PA6, increasing the heating rate as well as the cooling rate lowers both melting and crystallization peak temperatures (Fig. 3), but only by a few degrees (decrease of a maximum of 10 °C for a four times faster cooling rate at 80 bar (8 MPa)). Among possible explanations for these decreases, the accuracy of the measured temperature, especially at high heating or cooling rate, could be responsible for discrepancies of a few degrees. The fact that the system was only calibrated under atmospheric conditions could also explain the differences observed. But the main argument would be that, because of the hole in the lid of the crucible, the polymer loses a certain amount of water during each heating–cooling cycle. Consequently, the faster the cooling or heating rate and the higher the pressure, the less time there is for the vapour pressure to equilibrate or for the sample to crystallize or melt, thus the lower the corresponding temperatures.

As a standard procedure, the combination of a cooling rate of 10 °C min^{-1} and a subsequent heating rate of 20 °C min^{-1} was chosen.

Influence of pressure

As expected, an increase in the pressure from 1 to 80 bar (0.1 to 8 MPa) does not affect significantly the melting temperature or the crystallization behaviour (Fig. 4). This is in agreement with previous work[11,12] which showed that an increase in pressure of 100 bar (10 MPa) brings about a change in melting temperature of less than 2 °C.

Crystallinity

Under atmospheric pressure, the crystallinity of pure PA6 used in this study is approximately 30%. The determination of this value

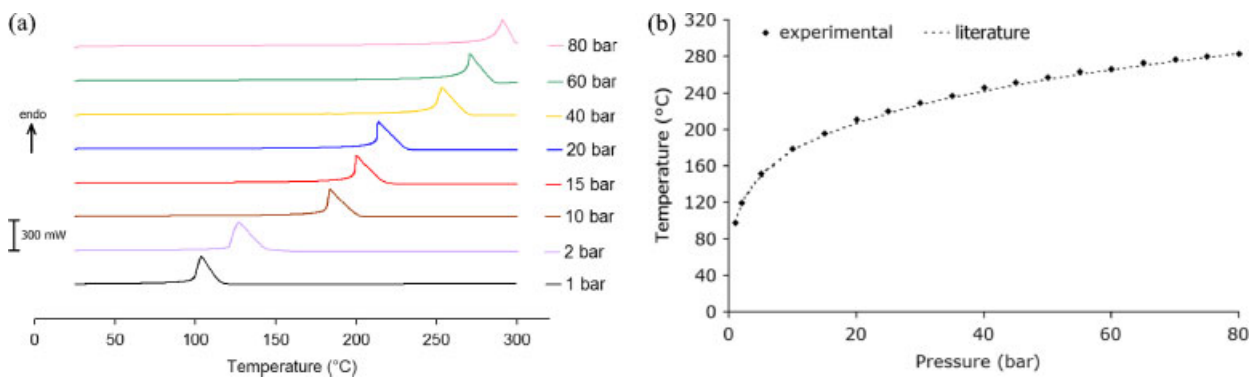


Figure 2. (a) DSC heating curves at 10 °C min^{-1} and (b) pressure–boiling onset temperature of distilled water.

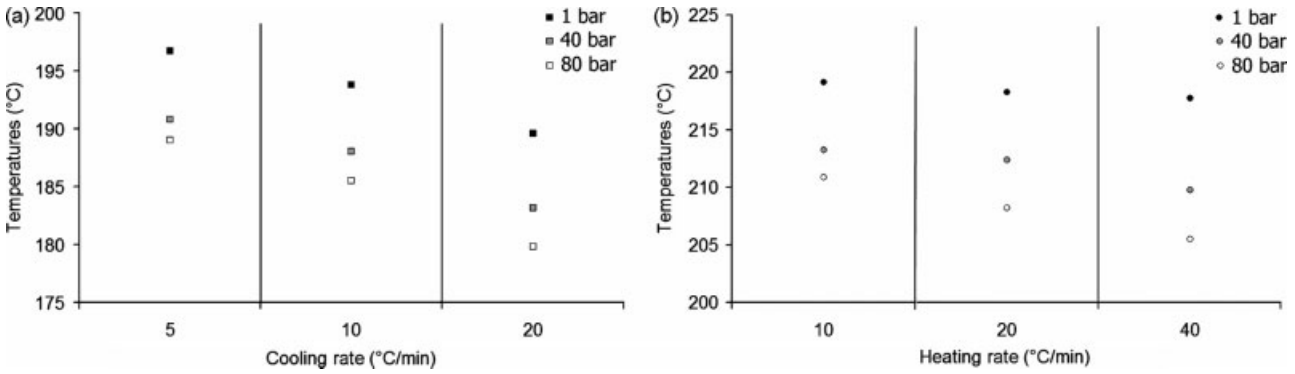


Figure 3. Influence at various pressures of (a) cooling rate and (b) heating rate subsequent to cooling (10 after 5, 20 after 10, 40 after 20 °C min^{-1}) on the crystallization and melting peak temperatures, respectively, for pure PA6.

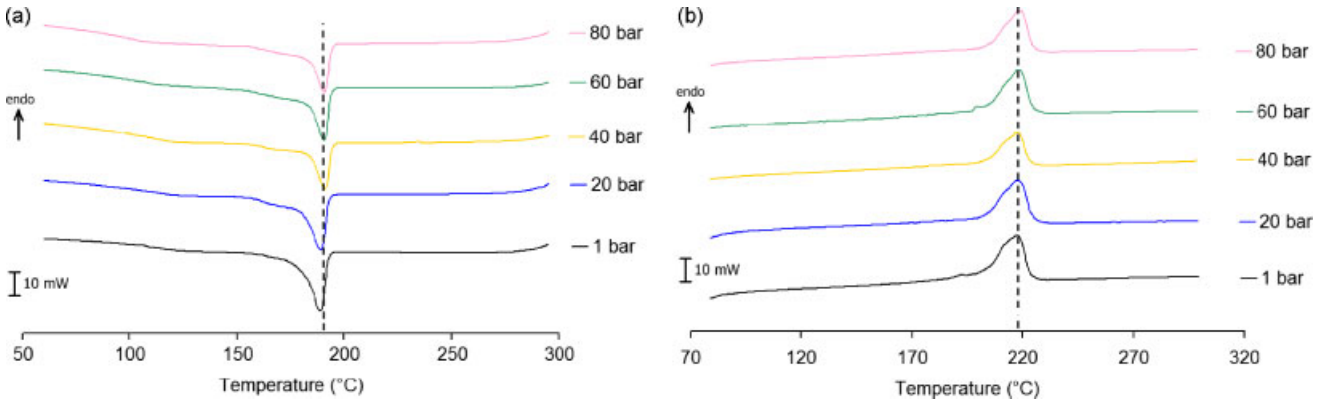


Figure 4. DSC curves of pure PA6 during (a) cooling at 20 °C min^{-1} and (b) subsequent heating at 20 °C min^{-1} as a function of pressure (mass of samples *ca* 15 mg).

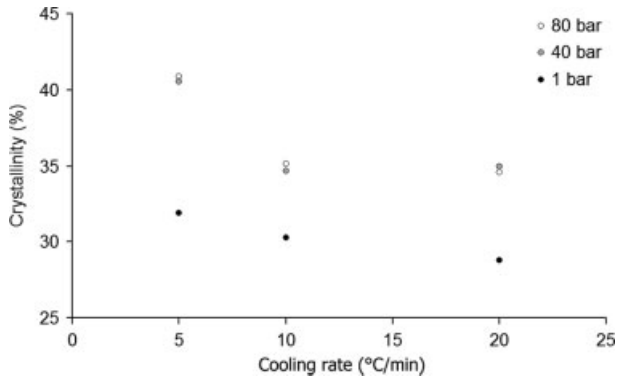


Figure 5. Crystallinity of pure PA6 cooled at various rates for various pressures.

was made using the STARe software according to the method described by Mathot[13] and used by Wevers and co-workers,[1–3] which takes into account the temperature dependence of the enthalpy of crystallization/melting. As soon as the pressure level is increased from 1 bar to a few tens of bars, the crystallinity increases to between 35 and 40%. This may be explained by the presence of 2.5% of water in PA6 (as determined using TGA) which remains liquid under these high pressures and helps crystallization to occur, whereas under atmospheric pressure, water evaporates.

In addition to the pressure level, the cooling rate notably influences the crystallinity: the highest value (40%) is obtained (as expected) for the lowest scan rate (Fig. 5). For cooling rates of 10 and 20 °C min^{-1} under pressures of 40 and 80 bar (4 and 8 MPa) the crystallinity drops slightly (to about 35%).

Summary of findings for pure PA6

From the results obtained, it is evident that the thermal behaviour of pure PA6 depends slightly on the sample morphology, a little more on the scan rates used but almost not at all on the pressure applied.

Addition of water to PA6

Influence of pressure

For a given PA6–water system, increasing the pressure from 20 to 80 bar (2 to 8 MPa) has almost no effect on melting temperatures nor on crystallization temperatures (Fig. 6), as expected; the major effect of pressurizing the system is easing the dissolution of PA6 in water, by keeping water in the liquid state. Under this condition, crystallization and melting temperatures of PA6 drop to 131 and 153 °C, respectively, i.e. application of pressure decreases the PA6 characteristic temperatures by almost 60 °C. For that, the pressure has to be just high enough to prevent water from boiling before the end of melting/dissolution has been reached. Thus, for a 50/50 mass% PA6–water system, the pressure should be higher than about 8 bar (0.8 MPa), as water then boils at 167 °C (Fig. 2(b)) while the PA6 under pressure dissolves in water up to an end melting temperature of approximately 165 °C (Fig. 6(b)). These results are summarized in Fig. 7.

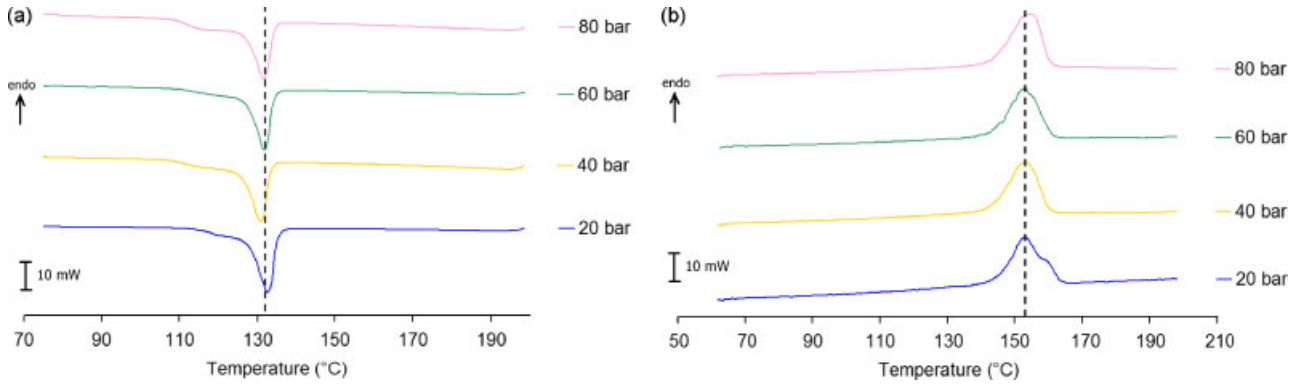


Figure 6. DSC curves at various pressures of a 50/50 mass% PA6–water system (a) during cooling and (b) subsequent heating, both at 10 °C min^{-1}.

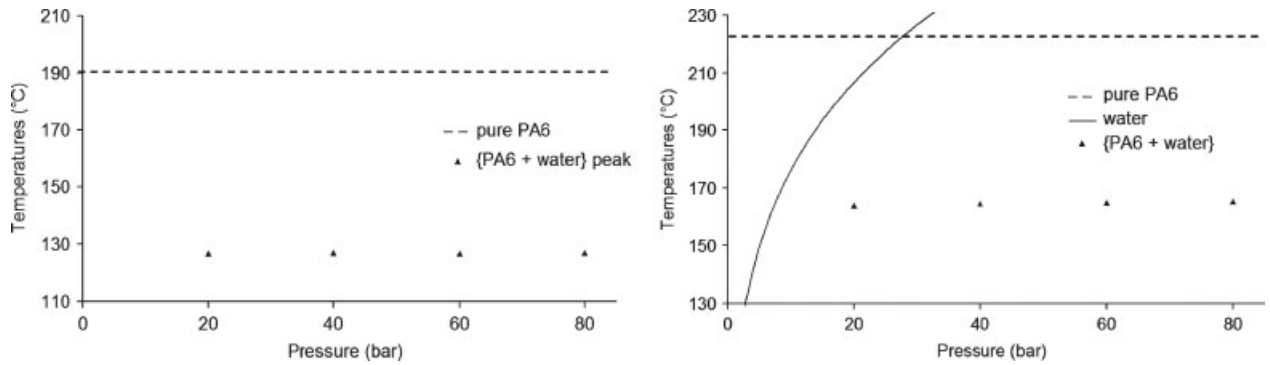


Figure 7. Influence of pressure on (a) crystallization and (b) end melting temperatures for pure PA6 and PA6 in a 50/50 mass% PA6–water system. The boiling curve of water is also shown in (b).

Effects of heating and cooling cycles on molar mass distribution

According to studies carried out by Wevers and co-workers[1–3] on PA6, the molar mass distribution of a 50% PA6–50% water system decreases after a heating–cooling cycle from 50 to 210 °C (the weight-average molar mass (M_w) changes from 31 to 22 kg mol^{-1} and M_w/M_n from 3.8 to 2.8). Even after four cycles a polymer still results. Such changes are comparable to the changes during processing, which are normal and accepted in practice. Moreover, an evaluation by SEC combined with viscosity measurements showed via the Mark–Houwink relation the absence of long-chain branching: after the cycles(s) the polymer is still linear.

Concentration of water needed for maximum temperature depression of PA6

Once the minimum pressure needed to observe the cryoscopic behaviour of PA6 had been determined, the concentration of water needed to get the maximum temperature depression of PA6 was studied. For this purpose, the relative amounts of water and PA6 added in the DSC crucible were calculated so that the total amount of material reached about 15 mg. The experiments were carried out under pressures of 20, 40 and 80 bar (2, 4 and 8 MPa), for various PA6 concentrations from 15, 43 or 21 mass% (i.e. dissolved condition) to 90 or 95 mass% (i.e. almost in the pure state).

At 20 bar (2 MPa), the peak temperature of crystallization of the PA6–water system stabilizes at *ca* 131 °C for PA6 concentrations of approximately 53 mass% and lower (Fig. 8(a)). The melting peak temperature of the same sample does not show any dependence on the PA6 concentration for approximately 66 mass% and lower, this temperature being *ca* 153 °C (Fig. 8(b)).

With respect to the range of concentrations where the crystallization and melting peak temperatures are constant, analogous results are obtained for pressures of 40 and 80 bar (4 and 8 MPa; Figs 8(c)–(f) and 9). Roughly speaking, the PA6 concentration characterizing the change to constant temperature (called the 'critical' PA6 concentration) varies between 65 and 75 mass%, irrespective of the pressure applied.

The critical PA6 concentration for crystallization is slightly lower than that for melting, which can be explained by the fact that a small loss of water may occur during the change from the cooling stage to the heating stage (due to the hole in the lid), by which the water concentration decreases and thus the PA6 concentration in the crucible increases. Overall, there is a loss of less than 0.2 mg of water between two cycles, which represents about 2 mass% of the total mass of the sample.

Explanation for the double peak at the critical PA6 concentration

Just below the minimum water concentration needed to obtain the lowest crystallization and melting temperatures (i.e. *ca* 30 mass%), the DSC heating curves generally exhibit double peaks (Figs 8(b), (d) and (f)). In order to understand the origin of these two peaks, experiments were carried out on PA6–water samples containing about 30 mass% of water. Each sample underwent four heating–cooling cycles, keeping the cooling rate constant at 10 °C min^{-1} and setting the heating rate at 20 (twice), 10 and 5 °C min^{-1}. The corresponding heating curves for two different samples are shown in Fig. 10.

Although the curves show some irreproducibility, in each case two melting peaks can be distinguished: a low-temperature one (*ca* 150 °C) and a high-temperature one (between 160 and 175 °C).

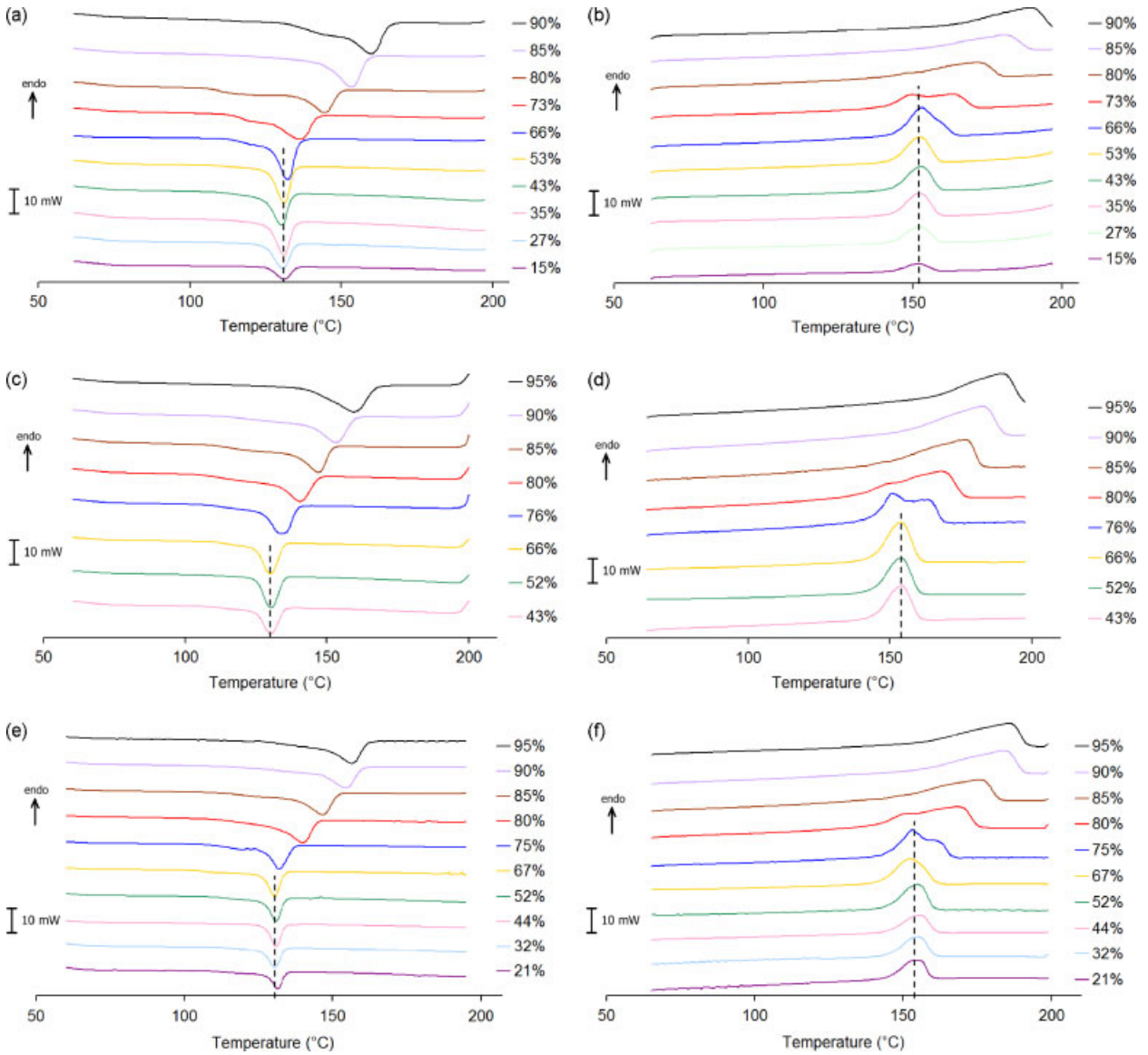


Figure 8. DSC cooling and heating curves at 10 °C min^{-1} of PA6–water systems at (a, b) 20 bar (2 MPa), (c, d) 40 bar (4 MPa) and (e, f) 80 bar (8 MPa) during (a, c, e) cooling and (b, d, f) re-heating as a function of PA6 concentration.

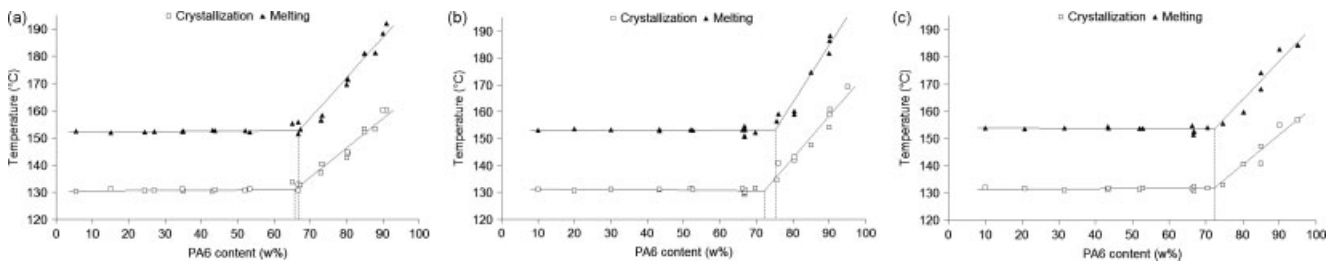


Figure 9. Influence of PA6 concentration on the crystallization and melting peak temperatures of PA6–water systems at (a) 20 bar (2 MPa), (b) 40 bar (4 MPa) and (c) 80 bar (8 MPa) from DSC cooling and heating curves at 10 °C min^{-1} (see Fig. 8).

When the heating rate changes, it can be seen that the relative importance of each of these two peaks changes: in the case of the highest rate, the lower melting temperature peak is predominant, while at the lowest rate the higher temperature peak prevails. This suggests that the melting behaviour is likely to be caused by recrystallization as relatively fast heating brings about an increase of the lower melting temperature peak (which is closest to the real melting temperature) at the expense of the higher temperature one because the time available for recrystallization is decreased (Fig. 10(a)). Conversely, slow heating promotes the strength of the higher melting temperature peak (which reflects re-melting subsequent to recrystallization) and by which the recrystallization

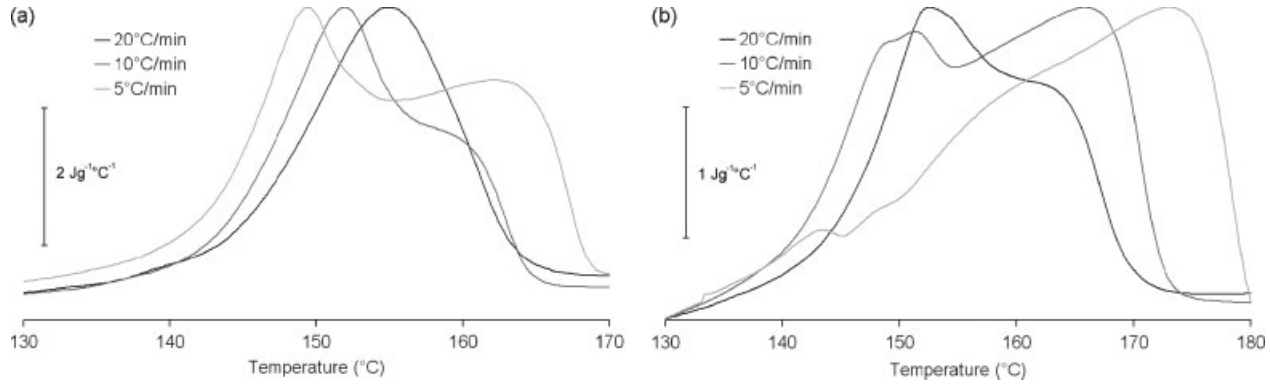
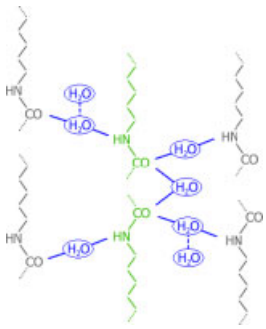


Figure 10. DSC heating curves of two different PA6–water systems containing 30 mass% of water, with heating rates as indicated subsequent to cooling at 10 °C min^{-1}. Data have been normalized to sample mass and heating rate in order to properly compare the shape of each curve.



$$\frac{n_{PA6}}{n_{H_2O}} = \frac{2}{3} \rightarrow \frac{m_{PA6}}{m_{H_2O}} = \frac{2}{3} \cdot \frac{113}{18} = \frac{113}{27}$$

$$\frac{m_{PA6}}{m_{syst}} = \left(1 + \frac{m_{H_2O}}{m_{PA6}}\right)^{-1} = \frac{113}{18} \approx 0.81$$

Figure 11. (a) Schematic representation and (b) corresponding equations for the sorption of water molecules on non-crystallized PA6 chains.

compensates part of the lower temperature melting peak, causing a lower intensity of this peak (Fig. 10(b)).

DISCUSSION

The progressive shift of the melting and crystallization temperatures towards lower values when water is added can be explained by the theory of the sorption of water in non-crystalline parts of PA6, established 40 years ago.[14] This theory claims that, for saturated conditions, three molecules of water are bound on two neighbouring amide groups. Thus, if two of these amide groups are considered (Fig. 11(a)), the first water molecule will form a double hydrogen bond between two carbonyl groups and thus is 'firmly bound'; then, more water molecules can join the already existing hydrogen bonds between carbonyl groups and hydrogen atoms of amide groups, leading to 'loosely bound' molecules, each one counting for half. As soon as these sites are all occupied, water molecules in excess will surround the others and link via van der Waals forces. This molecular ratio of three water molecules for two amide groups is equivalent to proportion of PA6 in the whole system of 81 mass% (Fig. 11(b)). Thus, this explains why, below this concentration, water is in excess and the crystallization and melting temperature depressions of PA6 are maximal.

This theory is confirmed by the study made by Wevers and co-workers on PA4.6.[1–3] It was shown that, for the experimental conditions chosen for the investigation, the polyamide concentration above which the melting temperature begins to increase is a little lower in the case of PA4.6 (*ca* 75 mass%) than in the case of PA6 (*ca* 85 mass%). This is in agreement with the discussion above as the theoretical ratio (PA4.6/syst) for saturated water conditions calculated using the equations shown in Fig. 11(b) only reaches 0.78.

The comparison between the results of this study and those of Wevers and co-workers[1–3] highlights the fact that compromises have to be made in order to characterize the PA6–water system using DSC, for example concerning the choice of the type of pans: in pressure-tight (closed) pans, the amounts of materials do not change, but the probability of leakage is high and there is no independency of temperature and pressure. In open pans, temperature and pressure can be independently adjusted, leading to more accurate peak values of melting and crystallization temperatures, but some water is likely to evaporate from the sample, and the amount lost can only be roughly estimated. Indeed, upon heating, in order to keep the pressure constant, some gas has to be released from the high-pressure DSC cell in which a limited amount of water vapour remains. This loss can explain the slight shift of the critical concentration as observed in Fig. 9, changing from cooling to heating, and also the dependence of the peak temperatures on the pressure applied. Nevertheless, the loss of water during the high-pressure DSC experiments only becomes significant when the PA6 concentration is above 65 mass%; below this concentration, water is in excess and the evaporation of a small amount of water does not influence the melting behaviour of PA6.

CONCLUSIONS

The crystallization and melting behaviour of PA6 under pressure has been investigated. The results show the influence of sample morphology, applied pressure and cooling and heating rates on the crystallization and melting temperatures, as well as on the crystallinity. The addition of a minimum water concentration to PA6 under pressure leads to a significant drop of the melting and crystallization temperatures. It has been shown that the conditions to obtain the maximum depression are a minimum water concentration of 30 mass% and a pressure of at least 8 bar (0.8 MPa; so that water remains liquid when the polymer melts).

The results of this study are likely to be useful for the construction of the PA6–water phase diagram. Moreover, the drop of the melting temperature of PA6 when water is added would help in the processing of composites,[15] especially in the case of temperature-dependent reinforcement materials such as natural fibres. Lastly, this paper thus confirms earlier research done by Wevers and co-workers[1–3] as well as the work done by Fedullo *et al.*[16] which highlighted the better compatibilization

and dispersion of montmorillonite charges in PA6 when water was added.

ACKNOWLEDGEMENTS

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