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Thermochimica Acta 453 (2007) 67–71
thermochimica acta
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Short communication

The way to measure quantitatively full dissolution and crystallization of polyamides in water up to 200 °C and above by DSC

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Received 10 July 2006; received in revised form 24 October 2006; accepted 26 October 2006
Available online 10 November 2006

Abstract

The way to measure quantitatively full dissolution and crystallization of polyamides in water up to 200 °C and above by DSC is described. Stainless-steel high-pressure pans enable research on fully dissolving polyamides in water under vapor pressure. The results show clearly that polyamide 6 (PA6) is soluble in water under vapor pressure in the whole concentration range and that water acts as a crystallization and melting point suppressor. The maximum temperature depression is approximately 60 °C. This depression of the transitions is independent of concentration over a large range (10–70 mass% PA6 in water). When PA6 dissolves in water during heating, the polymer often sets to the sides of the DSC sample pan. Because of this the contact between the sample and the bottom of the pan reduces during measurement and therefore DSC heating curves are frequently curved. Adding steel wool to these stainless-steel high-pressure pans improves the measurements by increasing the thermal conductivity between the sample and pan bottom, and as a result the DSC curves become less curved. The interpretation of the measurements improves and the possibility of reproducible peak area calculations also in heating comes in sight.

Keywords: Polyamide 6; Pressure; Steel wool; Water; Calorimetry; Crystallization and melting temperature depressions

1. Introduction

Instead of the frequently studied uptake of limited amounts of water in polyamides [1], we investigated fully dissolving polyamides in water. To this end, we used a concept developed at DSM Research in the early nineties [2–4] (and followed recently [5]): to dissolve polyamides in water and other solvents under pressure. Such a study of crystallization and melting/dissolution of polyamides like PA6 in the presence of water has not been published in the past—except for an indication by Murthy et al. who reported a melting point depression of 20 °C after annealing in water under pressure at 120 or 140 °C [6]. This dissolution in water decreases the melting- and crystallization temperatures drastically, as will be shown further on. The resulting crystallization- and melting temperature depressions realized in principle open new routes [2–4] to turn the negative aspect of water uptake into a positive one.

As is to be expected, dissolving PA6 in water during a DSC cycle causes a shift of the molar mass distribution to lower values as discussed in Ref. [4], because of shortening of the polyamide chains by scission. However, after a cycle still a polyamide results with a fairly high molar mass.

While the melting- and crystallization temperature depressions are observed clearly by DSC, it is also obvious that in these cases the DSC heating curves are quite often curved, while the DSC cooling curves sometimes show the same behavior, see Fig. 1.

Accordingly, quantitative interpretation of the melting and crystallization curves with respect to enthalpy changes is difficult, and especially crystallinity calculations in melting are not very reliable because of this curvature. Such curvature of the DSC curves occurs frequently in PA6–water systems and in polyolefin-dispersions-in-water systems [7] but sometimes it also takes place in pure PA6 [8,9].

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doi:10.1016/j.tca.2006.10.020

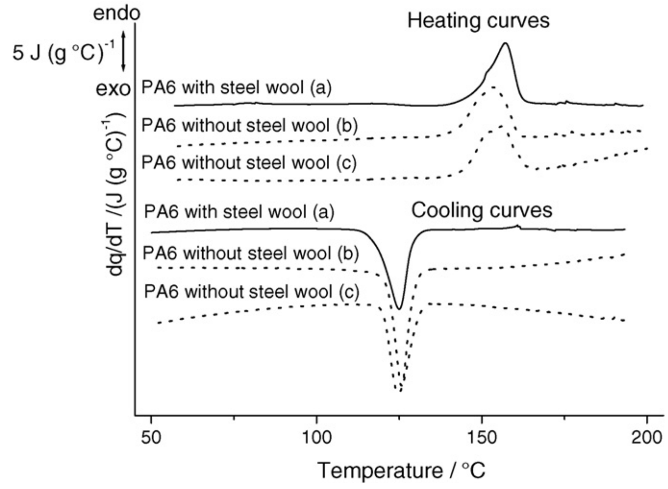

Fig. 1. First heating and first cooling DSC curves at 5 °C/min: representing (a) 19 mass% PA6 in water with steel wool (same as in Fig. 2), (b) 20 mass% PA6 in water without steel wool and (c) 17 mass% PA6 in water without steel wool (same as in Fig. 2).

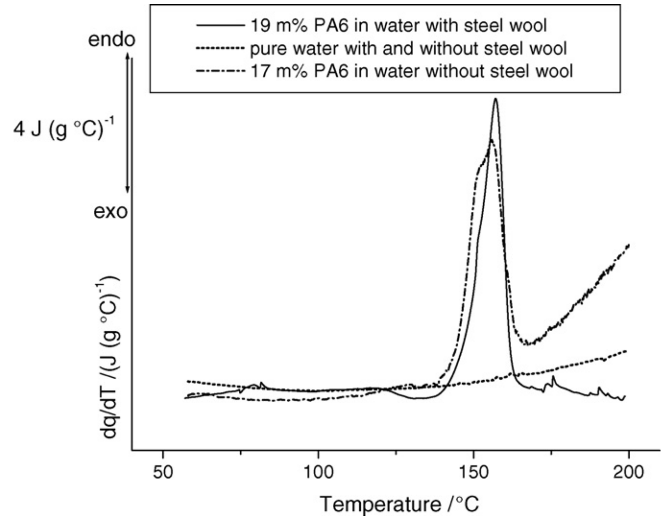

Fig. 2. First DSC heating curves of 19 mass% PA6 in water with steel wool, pure water with and without steel wool and 17 mass% PA6 in water without steel wool.

It is tempting to ascribe the curvature in case of heating a polymer–water system to evaporation of the water (in the closed cell), and in general of the solvent or low-molar mass liquid. However, that would not explain the occurrence of curvature in case of pure PA6 every now and then. Even so, water itself gives rise to some curvature; see the DSC curve of pure water with and without steel wool in Fig. 2.

However, in case of a PA6–water system, curvature is much more pronounced, as can be seen in the same Fig. 2. The strong increase at the highest temperatures is much stronger then to be expected for the PA6–water system. So, obviously, for the two reasons given, the major cause of curvature is somehow connected to the polymer itself.

Searching for the reason behind, a possible cause is found in the (changing) place of the polymer sample during measurement, resulting in a changing contact between polymer and pan bottom. Movement of the polymer sample is most probably related to aspects of the rheology of the polymer (whether it can flow or not under the measuring conditions) and to the balance between the surface free enthalpies of the polymer and the DSC pan (the material it is made of; its surface characteristics and its specific shape) used as driving force for movement. The melting- and crystallization temperature depressions in case of the systems we studied, like polyamide with water, ethanol, methanol, etc., have been measured using stainless-steel high-pressure DSC pans. When these pans are opened after measuring, we noticed that often the polyamide has been displaced to the sides and even to the top of the DSC pan, see Fig. 3 for an example. In this paper we suggest a solution for this problem.

2. Experimental part

2.1. Materials

The polymer used in this study is PA6, as produced by DSM, see Table 1, The PA6 granules were chopped into pieces before measurement. Demineralized water was used in the experiments.

2.2. Preparation and characterization of the samples

2.2.1. Measuring under vapor pressure

At 1 atm, water boils and evaporates at 100 °C. The vapor pressure of water – in a closed system – increases on heat-

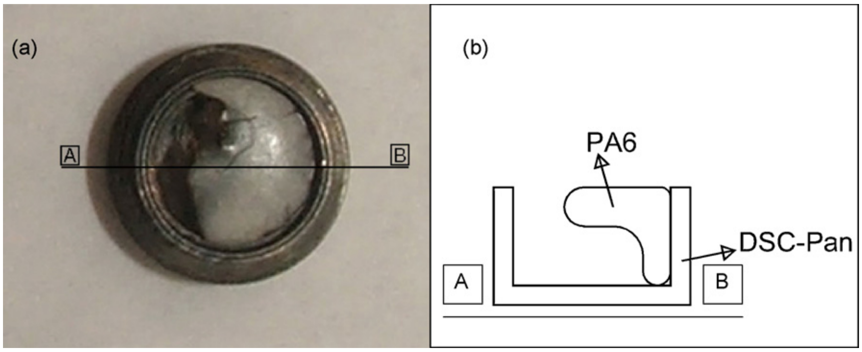

Fig. 3. Top view of a DSC pan of (originally) 70 mass% polyamide in water after a heating/cooling cycle (white/gray = PA6) (a) and schematic longitudinal section as clarification (b).

Table 1
Properties of the PA6 used in the experiments

Density at 23 °C (kg/m^3)	1130
M_w (kg/mol)	31
M_w/M_n	3.8
Melting peak temperature (°C) at 5 °C/min	222
Crystallization peak temperature (°C) at 5 °C/min	173

ing. When performing DSC measurements at temperatures higher than 100 °C, stainless-steel high-pressure pans (having a mass of approx. 600 mg) are needed withstanding vapor pressures up to a maximum of 27.9 bar at 230 °C for pure water [10].

2.2.2. Sample preparation and DSC measurements

A Perkin-Elmer Pyris 1 DSC was used to measure crystallization and melting behavior.

For PA6 up to 50 mass% (mass percentage) in water, the sample has been heated first from 50 °C to T_{melt} = 200 °C, followed by isothermal stabilization for 15 min and cooling to 50 °C, all scans at a rate of 5 °C/min. Above 50 mass% PA6 in water, to dissolve the polymer and also to avoid self-nucleation of the polymer, a T_{melt} of 30 °C above the dissolving end temperature was taken. The isothermal stabilization step of 15 min was chosen throughout on the basis of experiments varying stabilization times. After 15 min stabilization time – in contrast to shorter times – a single crystallization peak was observed instead of a double crystallization peak. Longer times for stabilization gave no further changes.

For the study of the influence of steel wool (obtained from the supermarket, having a circular cross-section with a diameter in between 0.02 and 0.06 mm) on the DSC curves, PA6 and water were brought together in a stainless-steel high-pressure pan at room temperature and then approx. 2 mg steel wool was added to this system. Subsequently the system was subjected to a DSC cycle. For all measurements an empty pan (without steel wool) was subtracted.

3. Results and discussion

3.1. Difficulties with measuring polyamides

As mentioned in the introduction, when PA6 dissolves in water, the polymer sets often to the sides of the sample pan and only a small amount of polyamide remains at the bottom of the pan, see Fig. 3 for an example.

Because of this, the contact with the bottom reduces during the measurement and as a result the DSC curves are frequently curved, especially in heating. In 47% of all the measurements without leakage (64 in total have been scrutinized) only the heating curve is curved, in 5% of the measurements only the cooling curve is curved, and in 17% of the measurements both the heating and cooling curves are curved. In 31% of the measurements there’s no curvature at all. Consequently, in quite a number of measurements interpretation of the melting and crystallization curves is hard, and as a result, e.g. crystallinity calculations are not very reliable because of this curvature. In an attempt to improve this unsatisfactory situation, we added a small amount of steel wool (approx. 2 mg) to the sample pan, as explained in the experimental section.

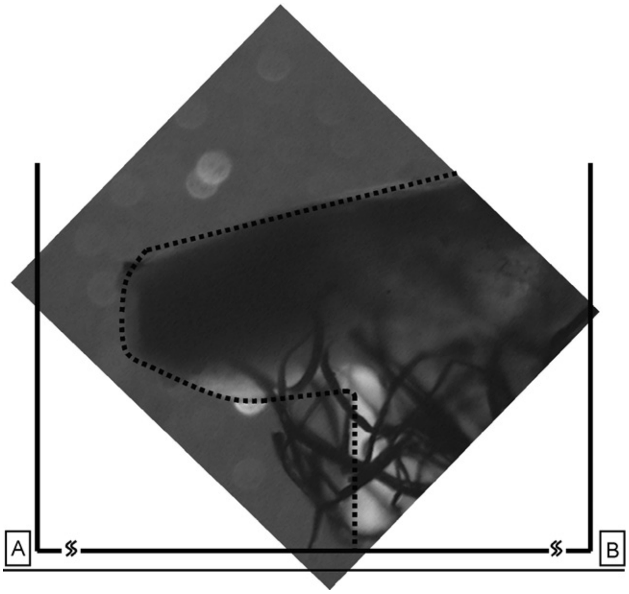

Fig. 4. Side view of the network of steel wool with the polyamide by optical microscopy. Black = steel wool, white/gray = PA6; contour of the PA6 roughly represented (as in Fig. 2) by a dotted line, and contour of the DSC pan by a solid line.

This steel wool forms a network together with the polyamide, as shown in Fig. 4 while the steel wool touches the bottom of the DSC pan.

Indeed, due to this, the thermal conductivity between the sample and the pan during measurement is improved and the DSC curves are less curved, as shown in Fig. 1. When measurements with steel wool and without steel wool are compared, there are also slight differences seen with respect to the DSC peak shapes. However, to our experience, these are related to the non-100% reproducibility of measurements on PA–water systems, and as such not caused by the use of steel wool. As a result, when the measurements of PA–water systems with and without steel wool are compared, we learn that with steel wool 67% of the measurements (12 without leakage in total), compared to 31% without steel wool, have no curvature. Nevertheless, 8% of heating curves; 0% of the cooling curves and 25% of both heating and cooling curves are still curved using steel wool. As such it is a clear improvement compared to PA6–water systems without steel wool where 47% of the measurements show curvature in heating, 5% in cooling and 17% in both heating and cooling.

When the same procedure (adding steel wool) is applied to pure PA6 in standard DSC pans, no improvements are visible. In both cases – with and without steel wool – curvature still poses problems. On the other hand, the results are not worsened either by adding steel wool: no differences with respect to, e.g. thermal lag are seen between the measurements with and without steel wool.

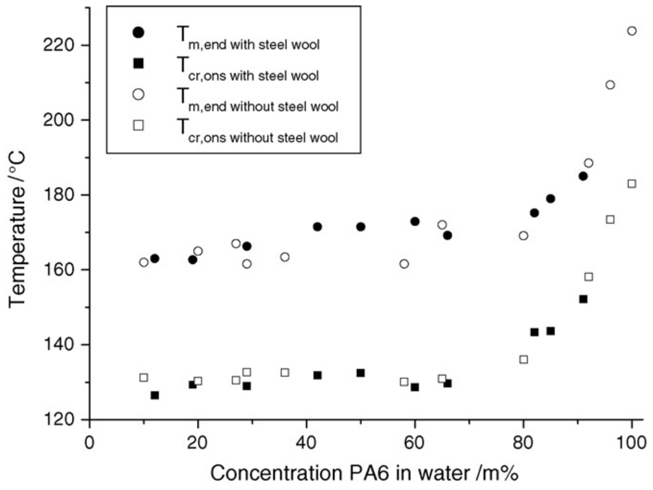

Fig. 5. Crystallization ($T_{\mathrm{cr,ons}}$) and end of melting temperatures ($T_{\mathrm{m,end}}$) from first heating and first cooling curves as function of the concentration of PA6 in water with and without steel wool by DSC at 5 °C/min.

Clearly, using steel wool in case of PA6–water systems the interpretation of the measurements improves and moreover, the possibility of reproducible conventional crystallinity calculations from heating curves comes in sight. By “conventional” is meant calculating crystallinity by drawing a line (arbitrary by necessity, see Ref. [11]) under the melting peak to obtain a peak area. Quantitatively temperature dependent crystallinity calculations [11] remain in both cases (with and without steel wool) not feasible.

3.2. *Dissolution and crystallization of PA6 in water*

Measurements of PA6–water in the whole concentration area have been performed before, see Ref. [4]. Water lowers the temperature of melting of PA6 radically and also any subsequent crystallization and melting with respect to temperature, see Fig. 5. Such depressions of the transition temperatures occur across the whole concentration range. The maximum depression of the crystallization and melting temperatures is approximately 60 °C (130 and 165 °C for PA6 in water compared to 184 and 227 °C for pure PA6 for onset of crystallization and end of melting, respectively). These temperature depressions of the transitions are more or less independent of the concentration over a large concentration range (10–70 mass% of PA6 in water). When these measurements are repeated with steel wool (only first heating and first cooling curves are presented here), we see – within the experimental error – no significant temperature differences between the different sets of measurements. The experimental error with respect to characteristic temperatures, like onset of crystallization ($T_{\mathrm{cr,ons}}$) and end of melting temperatures ($T_{\mathrm{m,end}}$), is appreciable especially for the first heating curves because the sample shape and the sample and/or thermal histories can be different. Besides, other parameters, like the absolute amount of water; the diffusion of water into the PA6, etc. play a role as well.

Finally, a few words to some peculiarities seen in Fig. 2. As mentioned, for a number of reasons, first heating curves of different, freshly prepared samples usually differ to some extent, as is explained at the evaluation of Fig. 5. First DSC heating curves also can show irregularities, e.g. see the “spike-like” phenomena in Fig. 2 for the 19 mass% PA6 in water with steel wool, hardly seen in the same curve in Fig. 1 because of different scale of the *y*-axis. Possible reasons are release of stresses within the sample; and changes of the sample, adjusting itself to a new shape and position throughout the heating ramp as outlined before. In addition, in between approx. 120–140 °C an exothermic phenomenon is seen, while at the low-temperature side of the melting peak a shoulder is seen. These phenomena will be discussed in subsequent publications.

4. Conclusions

DSC curves on polymers as measured bare, in solvents and in non-solvents often show curvature. It is recommended to open the pan afterwards and inspect the sample on possible changes with respect to its location as a possible cause. DSC measurements up to temperatures up to 200 °C and above on polyamides in water using stainless-steel high-pressure pans improve clearly when steel wool is added to the pan. Both the heating and cooling curves becomes less curved and conventional crystallinity calculations become more reproducible. Thermal lag is not influenced. As in the case without using steel wool, the results show clearly that PA6 is fully soluble in water over the whole concentration range and that water acts as crystallization- and melting temperature suppressor. Analogous results have been found for other polyamides, also in case of solvents like butanol, ethanol and methanol [2,4].

Acknowledgements

MW recognizes the European Community for a Marie Curie Industry Host Fellowship grant, contract no. HPMI-CT-2001-00112, through DSM Research. Prof. G. Groeninckx, Katholieke Universiteit Leuven, Leuven, Belgium is appreciated for his enduring support. MSc Eng J. Ibarretxe Uriguen, Lea-Artibai Ikastetxea, Markina-Xemein, Spain, is thanked for discussion.

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