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Thermochimica Acta 271 (1996) 1-8

thermochimica
acta

Simultaneous X-ray diffraction and differential thermal analysis of polymers[1]

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Received 8 May 1995; accepted 13 June 1995

Abstract

Simultaneous measurement of X-ray diffraction patterns and differential temperature curves is an excellent method to eliminate the disadvantages in common DSC analysis. Problems in DSC analysis of polymers include phenomena such as multiple melting and fractionated crystallization. By simultaneous registration of X-ray diffraction patterns the melting and crystallization peaks can be assigned to different phases in multiphase materials. A sample holder was developed which serves the requirements for simultaneous measurement of X-ray diagrams and differential temperature curves. The necessity for the development of the system is shown as well as details of the sample holder and test measurements on polyamides.

Keywords: Simultaneous XRD/DTA; Polyamide; Polymer blend

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1. Introduction

Investigation of the crystallization and melting behavior of polymer blends is often done by DSC analysis. Polymer blends are mostly heterogeneous materials and show a very complex crystallization and melting behavior which results in phenomena such as multiple melting and fractionated crystallization. But, because of the integral character of the DSC experiment, the various exothermic or endothermic peaks cannot be assigned to the different phases of the sample. In contrast to DSC, X-ray diffraction is a phase selective method and can be used advantageously for investigating phase transition phenom-

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[1] Presented at the 11th Ulm Conference, Freiberg, Germany, 29-31 March, 1995.

SSDI 0040-6031 (95) 02594-4

ena. Qualitative phase analysis by X-ray diffraction is based on Bragg's law which relates the diffraction angle θ to the lattice plan distance $d_{(hkl)}$ ((hkl) are the Miller indices of the lattice plan) (Eq. (1)):

$$2d_{(hkl)}\sin(\theta) = n\lambda \tag{1}$$

n is the diffraction order and λ the wavelength of the characteristic radiation used. In a multiphase material the integral intensity I of an interference diffracted by the phase i is proportional to the weight fraction X_i of this phase (Eq. (2)):

$$I_{(hkl),i} = \frac{K_{(hkl),i} \times X_i}{\rho_i \times (\mu/\rho)_\mathrm{m}} \tag{2}$$

ρ_i is the density of the phase i and $(\mu/\rho)_\mathrm{m}$ is the mass absorption coefficient of the mixture. $K_{(hkl),i}$ is proportional to the structure factor $F_{(hkl),i}$ which relates the intensity to the crystal structure [3].

To demonstrate the difficulties in DSC analysis of polymer blends in Fig. 1, DSC cooling runs of PA 6.10 and the blend PA 6.10/ABS 20/80 wt% (ABS; acrylonitrile–butadiene–styrene copolymer) are plotted. The DSC scan of PA 6.10 shows, as expected, only one crystallization peak at 461 K (maximum position), but the scan of the blend shows three crystallization peaks at different temperatures. ABS is not able to crystallize. The question is: what is the reason for multiple peaks during continuous cooling? Reasons can be a morphology-induced change of the nucleation mechanism [1,2] and the

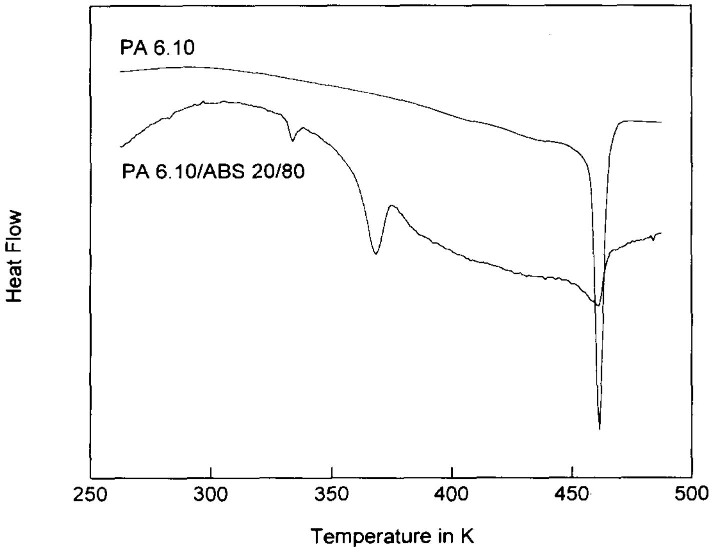

Fig. 1. DSC scans of PA 6.10 and the blend PA 6.10/ABS 20/80 wt% (-10 K min^{-1}).

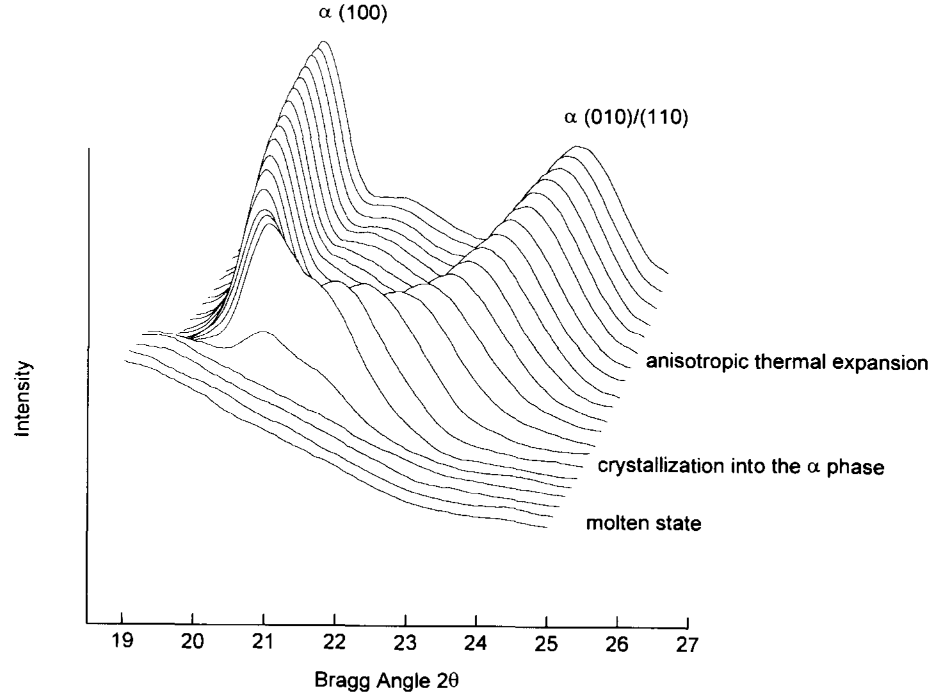

Fig. 2. XRD diagrams of PA 6.10 during continuous cooling (-10 K min^{-1}).

polymorphism of PA [4]. The X-ray diagrams $I(2\theta)$, which are dependent on temperature, indicate that the polymorphism of PA is the reason. The triclinic α phase shows two strong interferences at about 20 deg 2θ (100) and 24 deg 2θ (010)/(110), the nematic γ phase shows a peak at 21 deg 2θ. Fig. 2 shows the series of X-ray diagrams during continuous cooling with the same cooling rate as in DSC. The curve in front corresponds to the molten state. At 463 K two overlapping peaks arise which can be assigned to the α phase. Both peaks are shifting in opposite directions during cooling because of the anisotropic thermal expansion or the Brill transition [4]. In Fig. 3 the same experiment was performed with the blend PA 6.10/ABS. The peaks are very low in intensity due to the small amount of PA 6.10 in the blend. It is clearly visible that the material begins with the α crystallization process at the same temperature as pure PA 6.10, but at 373 K a third peak arises corresponding to the γ phase. So, we assume that the low temperature crystallization peak is caused by a crystallization into the nematic γ structure which is not observable in pure PA 6.10.

2. Experimental

Samples used in this work were polyamides from BASF (PA 6, PA 6.10) and ABS

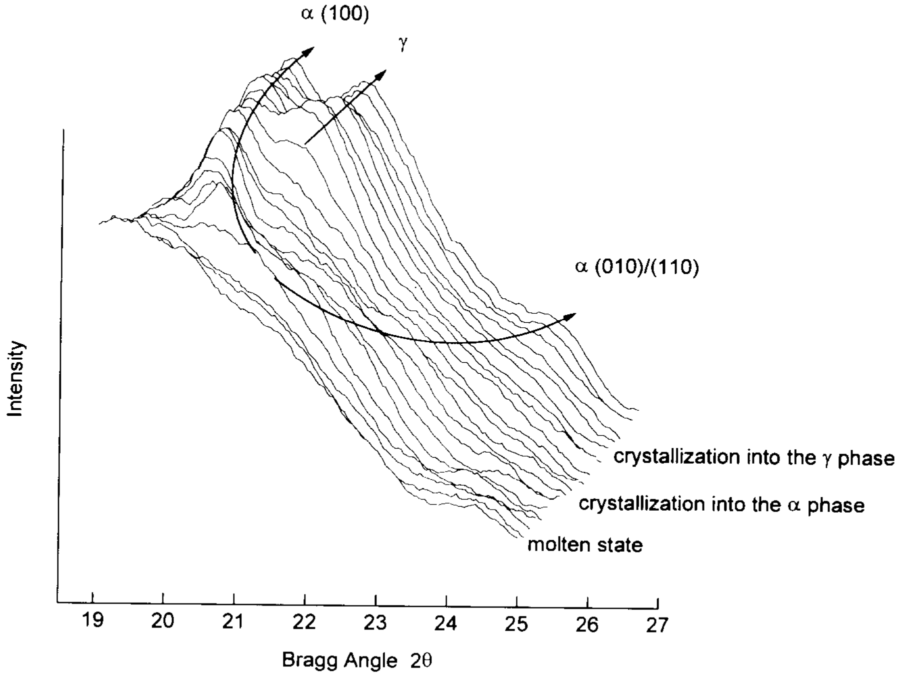

Fig. 3. XRD diagrams of the blend PA 6.10/ABS 20/80 wt% during continuous cooling (-10 K min^{-1}).

from BUNA GmbH. Blends were prepared by melt mixing in a single screw extruder followed by injection molding. Details of processing were described in Ref. [2].

DSC experiments were performed on a Perkin & Elmer DSC-2C in a nitrogen atmosphere. The weight of the samples was about 10 mg. The heating and cooling rate in all experiments was 10 K min^{-1}.

For X-ray diffraction experiments a diffractometer URD 63 (Seifert-FPM) in Bragg-Brentano geometry in combination with an IRIS generator (40 kV, 30 mA) was used. The wavelength of the radiation was 1.5418 Å (CuKα, Ni-filtered). For controlled heating and cooling, the sample was placed in a temperature chamber (Paar KG). The chamber was evacuated to minimize thermal and oxidative degradation. X-Rays were detected by a position sensitive detector (STOE). The detector (in the position fixed) facilitates the simultaneous measurement of 7 deg 2θ angular range with a resolution of 0.02 deg $\Delta 2\theta$ (diameter of the diffractometer circle was 360 mm). Typical counting times were between 15 and 60 s per diagram.

The XRD/DTA system was developed on basis of the diffractometer URD 63 and the TA Instruments TA 2000/DSC 910 system. A new sample holder which is compatible with both systems was constructed. The main item was a metallic cylinder with four drill-holes. The central hole was used for inserting a resistance heater. The three symmetrically arranged holes around the central hole were for the sample, a reference and a control thermocouple for the controller. Two slits were milled into the cylinder for the inci-

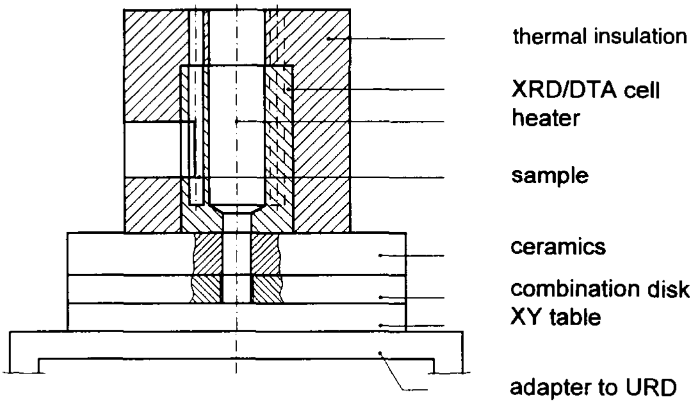

Fig. 4. Sample holder for simultaneous XRD/DTA.

dent and diffracted X-ray beam to pass. The sample was placed in a special glass tube with a low mass absorption coefficient or in aluminum foil. The cylinder was isolated by ceramics and teflon or mineral fibers depending on the temperature range used in the measurement (Figs. 4 and 5).

The temperature measurement of the sample and the reference was realized by Ni–NiCr thermocouples. The thermocouples were placed directly in the sample and the reference powder. Finely powdered quartz was used as reference. The problem in the sample preparation is the thermal contact between the sample and the thermocouple which is lost in the case of thermally induced macroscopic movements of the polymer powder. The grain size of powdered polymers (by grinding) is relatively large which leads to holes. These holes cannot be removed by compressing the material in the glass or alumi-

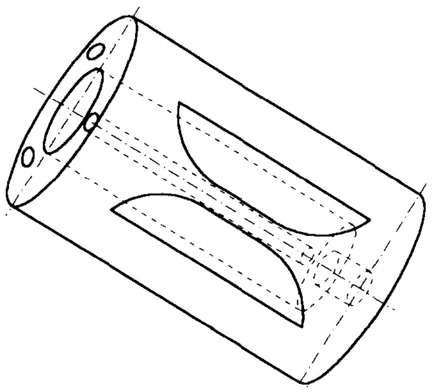

Fig. 5. Sample holder for simultaneous XRD/DTA (in perspective).

num tube. Therefore, it is better to use solid cylinders of the polymer with a special 0.25 mm drill-hole for inserting the thermocouple.

3. Results

Test measurements were carried out with extruded PA 6. The sample as bulk material was placed in aluminum foil and heated at 10 K min^{-1} from 293 K to 573 K. The simultaneously recorded $I(2\theta)$ diagrams and the DTA scan are shown in Fig. 6. The $I(2\theta)$ diagrams were registered with a fixed detector in the angular range from 18.5 to 25.5 deg 2θ and a counting time of 30 s per diagram. At a heating rate of 10 K min^{-1}, every 5 K an

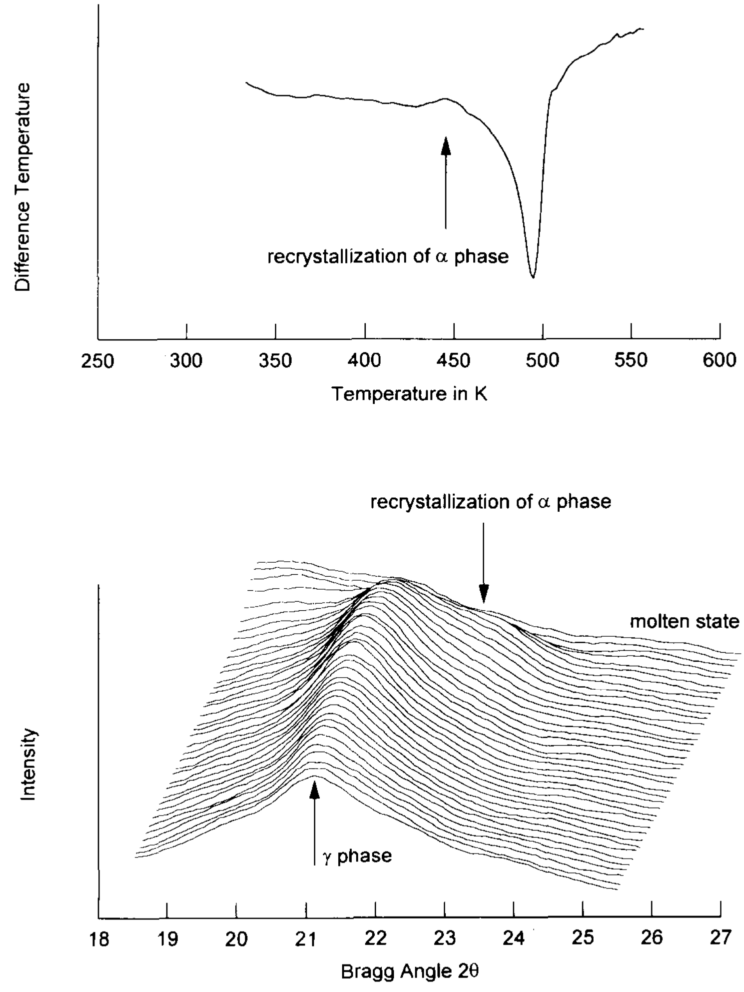

Fig. 6. Simultaneous XRD/DTA test measurement on PA 6 (+10 K min^{-1}).

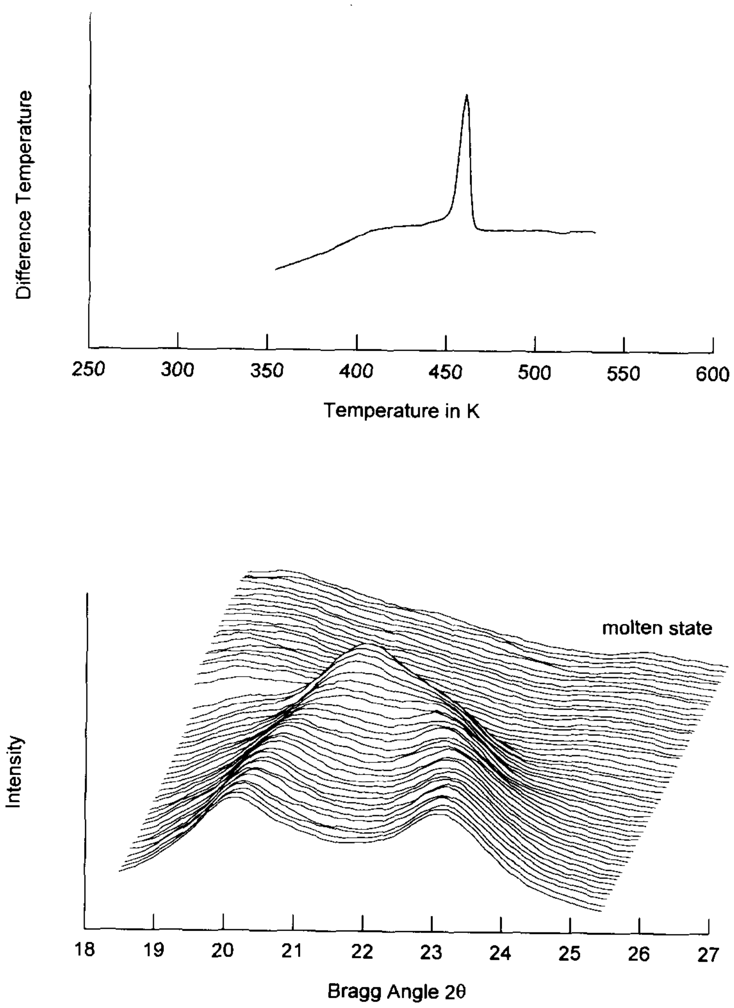

Fig. 7. Simultaneous XRD/DTA test measurement on PA 6 (−10 K min^{-1}).

$I(2\theta)$ diagram is available. It should be noted that counting times up to 10 s per diagram and lower are no problem in evaluating X-ray data [5]. The first X-ray-diagram shows that the material after extrusion into the water bath results in the γ structure which is indicated by the single peak at 21 deg 2θ. Shortly before the melting temperature is reached in the DTA scan, a small exothermic reaction is visible which can be interpreted as a recrystallization from the γ phase into the α phase. In the X-ray diagrams, a second peak appears at the same temperature at about 22 deg 2θ corresponding to α (020)/(220) interference. This result is in agreement with other experiments on the crystallization of amorphous polyamides where (1) crystallization from the amorphous material into the γ phase and (2) recrystallization from γ to α takes place [6]. The material was held in the molten state for 5 min before it was cooled at a rate of 10 K min^{-1}. At the crystallization temperature the exothermic reaction is visible in the DTA scan and in the parallel recorded $I(2\theta)$ diagrams, a peak arises from the amorphous background. As found in earlier investigations, the single peak is the high temperature form of the α structure. During cooling, the transition of the material to the low temperature form is indicated by a splitting into two peaks and contrary shift of the maximum positions takes place [4].

4. Conclusions

Test measurements on polyamides have shown the advantages of the combined XRD/DTA system compared to a single DSC analysis. The most important additional information by XRD is the correlation of DSC peaks to the transition of definite crystalline phases. Another advantage is the possibility of phase selective measurement of all interesting structure parameters evaluable from X-ray data as anisotropic thermal expansion or crystal morphology. The XRD/DTA system facilitates measurements in a temperature range from room temperature to 573 K and higher with a very high precision in temperature control and in combination with a PSD with heating rates which are usual in DSC experiments. Next, a new cell will be constructed for controlled cooling and a better baseline stability. The system will then be used for basic work in interpreting crystallization data including crystallization kinetics of PA blends measured with XRD, DSC and thermal-optical analysis.

Acknowledgements

The authors wish to thank TA Instruments for their generous support of this work. Special thanks are due to N. Gerhardt for his advice regarding construction of the sample holder.

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