The endothermic “annealing peak” of poly(phenylene sulphide) and poly(ethylene terephthalate)

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Abstract The appearance of an endothermic annealing peak in semicrystalline poly(phenylene sulphide) and semicrystalline poly(ethylene terephthalate) after annealing at or above the cold-crystallization temperature is investigated by temperature-modulated differential scanning calorimetry, thermomechanical analysis and dynamic-mechanical analysis. The results indicate relaxation processes in the interlamellar amorphous phase, which is in a strongly constrained state after cold crystallization. During the annealing treatments rearranging processes take place. These processes result in a separation of the amorphous phase into an interlamellar relaxed and a “pseudo-crystalline” phase.

Key words Poly(phenylene sulphide) – Poly(ethylene terephthalate) – Annealing – Thermal history – Crystallization

Introduction

In the past, numerous studies have been devoted to the correlation between thermal history, melting behaviour and morphology of poly(phenylene sulphide) (PPS) [1–7], poly(ethylene terephthalate) (PET) [8–14] and poly(ether ether ketone) [15–24]. After crystallization from the glassy amorphous state (cold crystallization) and subsequent annealing treatment between the crystallization and the melting temperature, changes in the amorphous phase take place. In differential scanning calorimetric measurements, an endothermic peak is found about 20 °C above the annealing temperatures (“annealing peak”). Until now many different kinds of measurements have been performed to understand the structural changes which take place during the annealing treatments [differential scanning calorimetry (DSC), temperature-modulated DSC (TM-DSC), dynamic-mechanical analysis (DMA), wide-angle X-ray scattering and small-angle X-ray scattering]. Five different models have been put forward to explain the annealing peak.

1. Different crystal morphologies [4–6, 18]. According to this model the dual melting endotherms found in DSC are due to the melting of two crystal populations of different morphologies. No reorganization from one population into the other is assumed.

2. Different populations of crystallite sizes [19, 20]. Primary crystallization forms larger crystalline lamellae compared to the lamellae formed during secondary crystallization. The secondary formed lamellae melt first at lower temperatures and give rise to the extra melting endotherm in the DSC scans.

3. More or less perfect crystals [1, 3]. A second, less perfect pseudo-crystalline phase is induced on annealing. This phase melts just above the annealing temperature at which it was formed.

4. Crystal perfecting by melting and recrystallization [9, 10, 12, 13, 15, 16, 21, 23–25]. The “annealing peak” phenomenon is related to morphological changes in the microstructure of the semicrystalline samples during the DSC scan. Melting of the initial crystal morphology happens, which is characteristic of the previous crystallization history of the sample. The “annealing peak” is then indicative of the onset of melting of these crystals. In the temperature interval between the annealing and the final melting peak, all the crystals experience a continuous melting and recrystallization process.
5. Three-phase model [14, 27, 28]. In this model, the crystalline/amorphous interface is considered to be a “rigid amorphous” phase and separates the lamellar crystals from the amorphous areas.

None of the models fit with all the experimental results. It is the purpose of this paper to present some new results from TMDCS, thermo-mechanical analysis (TMA) and DMA. It will be demonstrated, that the three-phase model consisting of one crystalline but two amorphous (“pseudo-crystalline” and relaxed) phases explains our results best.

Experimental

Materials and sample preparation

Isotropic sheets of amorphous PET (Hostaphan, thickness 130 µm) and PPS (Litex-P, thickness 105 µm) were kindly supplied by Kalle-Hoechst (Germany) and PCD-Polymers (Austria), respectively.

All heat treatments were carried out in an oven.

Isothermal crystallization of these amorphous sheets was performed at \( T_c = 134 \)°C for 90 min for PET and at \( T_c = 129 \)°C for 45 min for PPS.

Subsequently, isothermal annealing \( (T_a) \) was performed on the semicrystalline samples at \( T_m > T_a > T_c \) with \( T_a = 134 \) and 154°C for PET, and \( T_a = 129, 155 \) and 180°C for PPS. The annealing times ranged from 24 to 552 h.

Temperature-modulated differential scanning calorimetry

The device used was an MDSC 2910-system from TA Instruments coupled with a TA 2000 control system. All measurements were performed with a heating rate of 5 K/min having a period of 60 s and an amplitude of 0.796 K. The input of the three parameters are visualized in a simple mathematical description of the heat flow

\[
\frac{dQ}{dT} = \frac{dF}{dt} \left[ C_p + f_v(t, T) \right] + \frac{dF}{dt} f_s(t, T) \tag{1}
\]

with

\[ \frac{dQ}{dT}, \quad \frac{dT}{dt}, \quad t, \quad C_p, \quad f_v(t, T), \quad f_s(t, T) \]

\( t \): time

\( C_p \): heat capacity

\( f_v(t, T), f_s(t, T) \): functions of time and temperature (kinetic answer)

Equation (1) implies, that the total heat flow is composed of a heat-capacity-proportional reversing part and a nonreversing part resulting from kinetic effects. The overall heat flow can be used to analyse complex events such as melting/recrystallization processes.

The heat capacity calibrations were performed with sapphire as a standard. Nitrogen was used for all measurements in order to avoid oxidation. The weights of the samples were 4.6 mg for PET and 3.5 mg for PPS.

Dynamic-mechanical analysis

A dynamic-mechanical analyser 2980 system from TA Instruments was used. All measurements were performed in a multifrequency mode with frequencies of 1, 2, 4, 8 and 16 Hz. The sample dimensions were 7 mm in length and 5 mm in width. An amplitude of 20 µm was chosen in order to guarantee a deformation within the linear response regime.

Thermo-mechanical analysis

The thermo-mechanical analyser 2940 system from TA Instruments coupled with a TA Thermal Analyst 2000 control system was used for the TMA measurements. TMA measures changes in the dimensions of a sample as a function of time, temperature and force (in our case as a function of temperature and a weak constant force). A “thermal expansion coefficient” \( (\alpha) \) of the samples was calculated from the temperature-dependent dimensional change using the expansion as well as the film/fibre mode. The expansion is measured under compressional stresses and primarily designed to determine the thermal expansion coefficient and the glass-transition temperature. The film/fibre mode is a tension mode. It is used for investigating thermal histories of films and fibres.

For the film/fibre mode the samples were 2.54 mm in width and 17.5 mm in length and the thickness was as supplied (PET: 130 µm, PPS: 105 µm). All measurements were performed with heating rates of 3 K/min.

Results

Temperature-modulated differential scanning calorimetry

Crystallinity

The samples were annealed at the crystallization temperatures \( (T_c) \) till no measurable increase in crystallinity \( (\chi) \) occurred (0.41 for PET and 0.38 for PPS after 90 min, respectively). Subsequently, the annealing treatment, causing the annealing peak, was performed for different times and temperatures. The crystallinities \( (\chi) \) were determined from the DSC measurements using the melting enthalpy \( \Delta H_m \):

\[
\chi = \frac{\Delta H_m}{\Delta H_{m0}},
\]

where \( \Delta H_{m0} \) is the specific melting enthalpy.

The values for \( \Delta H_{m0} \) were taken from the literature: \( \Delta H_{m0} \) (PET) = 119.8 J/g [8]; \( \Delta H_{m0} \) (PPS) = 112 J/g [26]. The respective crystallinities of the PET and PPS samples are presented in Tables 1 and 2.

| Table 1 | The crystallinity of annealed poly(ethylene terephthalate) for different annealing temperatures |
|---|---|---|
| \( T_a \) (°C) | \( \Delta H_m \) (J/g) | \( \chi \) |
| 134 | 48.9 | 0.41 |
| 154 | 51.0 | 0.42 |