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OPTICAL TRANSMITTANCE THERMAL ANALYSIS OF THE POLY(ETHYLENE TEREPHTHALATE) FOILS

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Abstract

The optical transmittance of poly(ethylene terephthalate) foils has been investigated using the linear heating as well as the isothermal heating. It was found out that transmittance records obtained at linear heating show the crystallisation and melting processes distinctly. These results are in accordance with those achieved by DSC measurements. The isothermal heating was especially applied to investigate PET cold crystallisation. In its course the optical transmittance first decreases to a certain minimal value, regaining some of the transmittance in the final period of crystallisation (crystal growth). The used method is suitable for investigating crystallisation processes of polymers accomplished at very slow rates.

Keywords: crystallisation, melting, optical transmittance thermal analysis, PET foils

Introduction

DSC is a standard method to investigate thermal behaviour of either pristine or filled polymers, irrespectively to their transparency. Less standard, but still highly diversified are thermo-optical methods of investigation. Some of them include microscopy (hot stage) methods with visual, or video viewing of the sample, some among them with manual temperature control. At present, we use the method, by which the optical transmittance (OT) of samples is evaluated as a physical parameter of the system. We prefer to call it the optical, or optical transmittance thermal analysis. It bears some common features to the optical methods given in [1–4]. From the other side, it may be ruled into a group of the newly emerged 'light beam', predominantly high temperature methods (the time resolved reflectivity of a laser beam [5], elastic light scattering [6], and measurement of thermal and optical properties of materials with a simultaneous non-contact monitoring of their shrinkage [7]). Recently it has been applied to investigate the high-temperature processes [8–11].

It is obvious that the samples to be investigated by this method need to be at least marginally transparent, at least at some temperatures of interest. The polymer films, due to their shape and transparency are especially suitable for thermal studies in transmitted light. Melting, growth or a rearrangement of the crystal-like lamellar or spherulitic entities bring about light scattering, attenuating thus the received light in-

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tensity. In this paper we record the optical transmittance changes of poly(ethylene terephthalate) (PET) foils during their heat treatment. PET was selected as a model material for its visually well-observed loss of transparency in cold crystallisation.

Experimental

Materials

Poly(ethylene terephthalate) homopolymer (Slovmer) was supplied by Slovensky hodvab, Senica. It contained no additives, with maximum ethyl ether extract 0.2%. Preparation of 800 μm thick foils was carried out using pilot scale twin extrusion followed by casting on a cold roll mill. The square test pieces (8×8 mm) were cut out from the casting foils.

Measurements

PET foils were placed on a 'microscopy' slide glass positioned onto a 2 mm thick, circular steel plate sample support inside the electrical furnace. The steel plate has an orifice of 4 mm in. The thermoanalytical device was briefly described elsewhere [8–11]. It consists of the temperature controlled electrical furnace, light source with a beam to pass the sample perpendicularly and Si-photodiode sensor to evaluate the light intensity (Fig. 1). The high efficiency red light emitting diode (LED) is used as a light source. The measured OT values are expressed in arbitrary units since the incident light intensity can be set to some proper value by the receiving camera apperture. The temperature control and data acquisition is carried out by software running under Windows 'on PC'. The temperature was measured by Pt–Pt/Rh thermocouple, calibrated in situ by melting point of benzoic acid (reagent grade chemical, Lachema Brno, melting point 122.3°C). The thermocouple junction was touching the steel plate support in a vicinity of the sample.

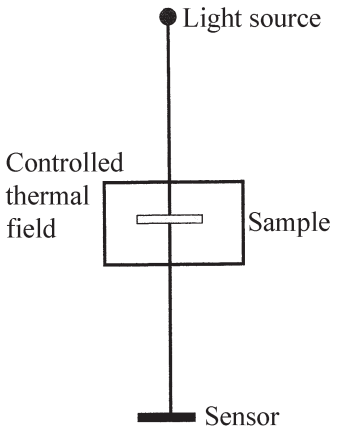

Fig. 1 Scheme of the experimental setup of optical transmittance thermal analysis (OTTA) device

Differential scanning calorimeter DSC-7 Perkin Elmer was used for DSC measurements. The temperature scale was calibrated using the standards In and Zn. The mass of samples was 3–4 mg. The samples were crimped in standard aluminium pans where an empty pan was used as a reference. The purge gas used was nitrogen.

The room temperature UV/VIS transmittance was measured using UNICAM HELIOS α 2.03.

Results and discussion

PET foil transparency at room temperature, measured by UV/VIS, is depicted in Fig. 2. The light emitting diode (LED) used in our apparatus is not a strictly monochromatic light source. Its spectrum shows a peak at approximately 720 nm (see insertion in Fig. 2). Figure 2 also shows that along LED wavelength spectrum (dotted line) the foil transmittance remains practically constant at room temperature.

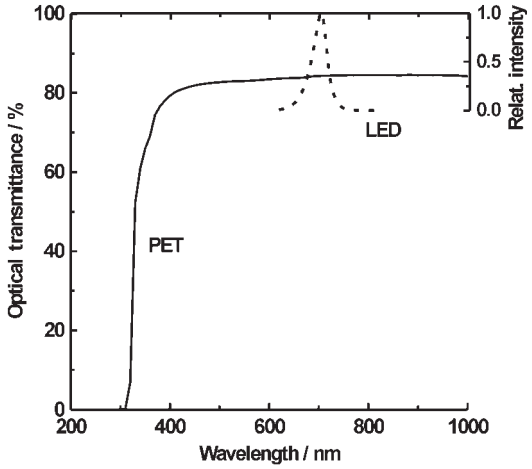

Fig. 2 Room temperature UV/VIS transmittance of the PET foil with an inserted spectrum of the light source (LED)

Heating of PET foils at a linear heating rate

The changes of the light transmittance of PET foil, recorded at a heating rate of 10 K min^{-1}, are compared to DSC record (Fig. 3). The optical transmittance relates to the left ordinate, whereas the DSC signal to the right ordinate. The deflection on DSC curve at 125°C corresponds to the cold crystallisation of PET [10] which, after its completion, renders the sample visually fully opaque. The corresponding complete loss of the PET foil transparency is clearly seen on the bottom curve of the optical transmittance record. As it is evident from the DSC curve, the cold crystallisation occurs in two steps. When measured by DSC, the cold crystallisation of PET is accomplished within the interval of 115–145°C, but in the interval 125–138°C when recorded by OTTA.

The optical transmittance curve shows a sharp peak at temperatures corresponding to PET melting. Similarly to the cold crystallisation, the melting occurs in a narrower temperature interval than observed by DSC.

The optical transmittance curve in Fig. 3 was measured up to 550°C. At 400°C, the sample becomes transparent again. By its visual inspection, the bubbles ascending in the polymer melt were formed, obviously due to PET thermo-oxidative degradation. The subsequent complete loss of the transmittance at higher temperatures was caused by a formation of carbonaceous decomposition species.

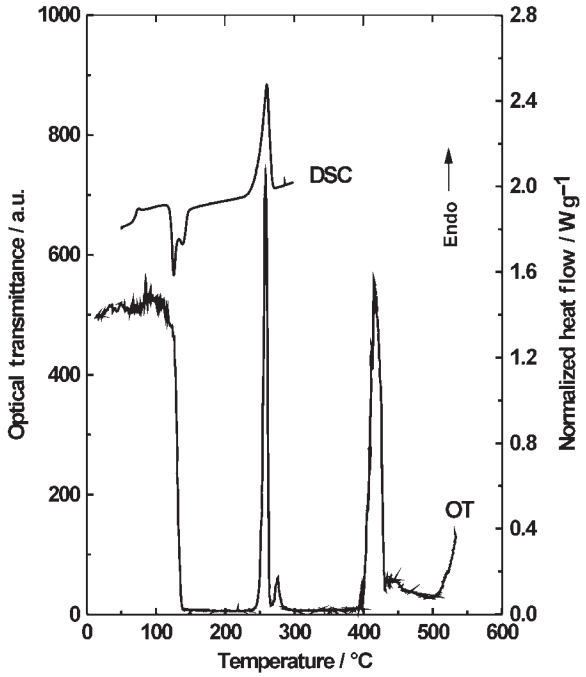

Fig. 3 Comparison of the optical transmittance (OT) and DSC records of the PET foil samples

OT record of Fig. 1 can be compared with reflected light intensity curve of the PET sample (Fig. 1 of [4]) as well as with the transmitted light intensity curve, referred to the polarised light [2]. The method applied in [4], similarly to our case, well describes PET cold crystallisation and melting. After the end of melting the light intensity remains, however, on the 'high' value. The sudden decrease of the transmittance above 260°C may mean the change in a shape of the sample because of the melt surface tension. The sample attains thus the light reflecting convex surface. Another reason may be the dynamic light scattering. In contrast, the thermo-optical investigation of the scratched PET sample [2] was sensitive to detect the glass transition temperature, but less sensitive to the PET cold crystallisation and melting process.

Isothermal heating of PET foils

In these experiments the cold crystallisation of PET foils was induced and accomplished at specified temperatures (Figs 4 and 5). The rate of heating to the selected constant temperature was 10 K min^{-1}. The zero time corresponds to the start of the ex-

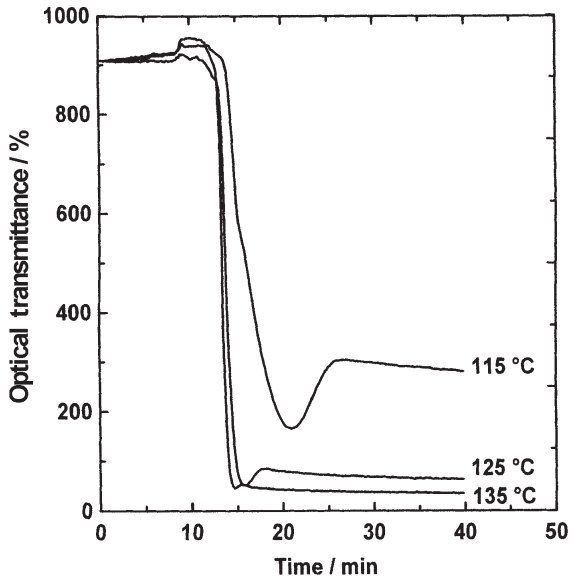

Fig. 4 Optical transmittance changes at isothermal crystallisation of PET foil samples (higher temperatures of crystallisation)

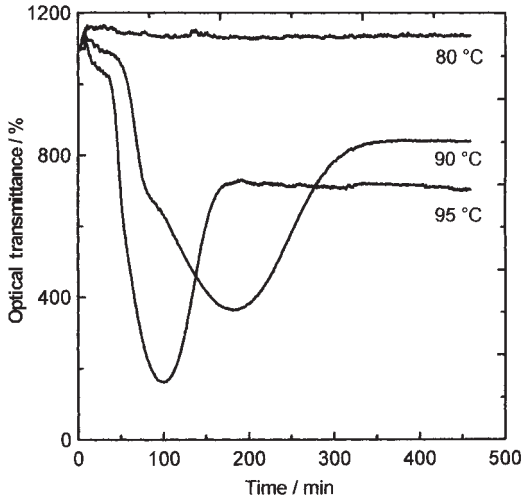

Fig. 5 Optical transmittance changes at isothermal crystallisation of PET foil samples (lower temperatures of crystallisation)

periment. All the curves exhibit a shoulder indicating the presence of two-step cold crystallisation, seen in DSC measurement at linear heating.

All records show an OT decrease and then a subsequent partial recovery of OT at later periods of the crystallisation. According to our preliminary scanning electron microscopy measurements, the cold crystallisation of PET samples is actually a spinoidal phase separation. The increase in the transmittance and the following reaching of steady state value in later periods of the isothermal crystallisation then may be associated with the growth of the separated phase domains. The minima on the transmittance curves can be explained by the effective domains size approaching the wavelength of the light radiation used.

Conclusions

It was found out that the investigation of the optical transmittance with temperature provides relevant information on crystallization and melting processes of PET foils. The results are fully in accordance with those achieved by DSC measurements.

The possibility to follow the processes with extremely slow rates, e.g. the very sluggish crystallisation courses is of special importance. An evaluation of the morphologies associated with specific points on OT curves as well as the computations to derive the activation energy of the PET isothermal crystallisation, based on the optical transmittance data are in progress.

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