



Analysis Method

DSC/SAXS analysis of the thickness of lamellae of semicrystalline polymers-restrictions in the case of materials with swollen amorphous phase

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ABSTRACT

Due to the simplicity and speed of the analysis, calorimetric (DSC measurements and Gibbs-Thomson method) or x-ray methods (SAXS measurements and Bragg's law or correlation function method) are the most frequently used in determining the thickness of crystals. This paper revealed that the direct application of the above mentioned methods in order to analyze the lamellar structure of semicrystalline polymers, the amorphous phase of which was swollen, may lead to incorrect results. Swelling of the amorphous phase (without changing the thickness of crystals) leads to a shift of the observed melting temperature towards lower values, what in turn will result in underestimated values of thickness of crystals, in the case of calorimetric method. At the same time, an increase of the value of long period is observed, what in turn will result in overestimated values of thickness of crystals, in the case of classical x-ray method (with the use of value of long period estimated according to the Bragg's law and crystalline volume fraction). We have observed that only the analysis of x-ray data with the use of the correlation function method enables to obtain actual values of the thickness of lamellar crystals of the polymeric materials with swollen amorphous phase. The means for correct analysis are pointed out. The above effects have been presented on the example of model, miscible, non-cocrystallizing semicrystalline polymer/low molecular weight modifier systems.

1. Introduction

The ability of a given polymer to crystallization process substantially affects its final physical and mechanical properties. During the crystallization process most of semicrystalline polymers, the lamellar crystals, the thickness of which is significantly smaller (usually by order of magnitude) than other dimensions (in the growth or lateral directions), are being generated. The thickness of lamellar crystals of a given material is a result of its chemical structure and the kinetics of crystallization and more importantly affects selected properties of a given polymer (mechanical, thermal). A correct analysis of lamellar structure (including information on the thickness of lamellar crystals) constitutes an important element of an overall analysis of the structure of a given semicrystalline polymer. Therefore, several experimental techniques were proposed, which allowed to determine the value of thickness of the lamellar crystals of semicrystalline polymers: differential scanning calorimetry (DSC) [1–3], small angle X-ray scattering (SAXS) [4,5], transmission electron microscopy (TEM) [6] or Raman spectroscopy (LAM) [7].

Due to the simplicity and speed of the analysis, the calorimetric method is a commonly used technique to determine the thickness of the

crystals of semicrystalline polymers. In this method the melting temperature of lamellar crystals (determined from DSC thermogram) is transformed into a lamellar thickness value by using the Gibbs-Thomson equation [8]:

$$L = \frac{2\gamma_e}{\Delta H_m^0} \frac{T_m^0}{T_m^0 - T_m} \quad (1)$$

where L is the thickness of lamellar crystals, T_m is the melting temperature of a lamellar crystals, T_m^0 is the equilibrium melting temperature of an infinite crystal, γ_e is the surface energy of the basal surface of a lamellar crystal and ΔH_m^0 is the enthalpy of fusion for the lamellar crystal.

Application of a classic calorimetric method in determining the thickness of lamellar crystals (or distribution of the thickness of lamellar crystals) usually results in overestimated values. Heating process of the material during a typical DSC measurement may be accompanied by several processes/phenomena (such as: superheating effects, melting kinetics, structure reorganization process (annealing, insufficient consideration of cold crystallization process) or thermal lag) negatively affecting the reliability of final results. The above mentioned processes/phenomena were analyzed in details in a past by Wunderlich and others

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[1,9–12].

Concomitantly, the attempts to eliminate or minimize the above mentioned effects/processes with use of new technical solutions and correction of experimental data were taken. In order to eliminate the cold crystallization effects and reorganization processes of lamellar structure of drawn polyamide 6 fibers Todoki et al. [13,14] exposed the samples to γ -rays in acetylene gas to introduce cross-links into the interlamellar regions. Unfortunately, the above method can be used only in case of polyamides and additionally it required chemical and physical modification of analyzed material.

A very important step in determining the actual melting temperature of lamellar crystals (and so their thickness) was applying fast scanning calorimetry (FSC). This technique, originally proposed by Schick et al. [15] has recently been commercialized [16]. A thorough analysis of this method presented in the papers [16,17] indicates the absence of cold crystallization effects and reorganization processes of lamellar structure during heating with the use of FSC. Furthermore, the studies presented by Toda et al. [18,19] indicated that thermal lag during fast heating measurement can be negligible if the sample thickness is sufficiently low (e.g., below 1 μm). The paper [3] includes the above mentioned factors and, what is more, in order to eliminate the process of superheating additional correction of experimental data was performed by deconvolution of the FSC curve using the calculated melting kinetics of single-sized lamellae consisting of folded-chain crystal. This enabled the authors of the paper to determine the actual lamellar thickness distribution of not-reorganized linear polyethylene. Determination of the actual thickness of lamellar crystals of semicrystalline polymers with the use of calorimetric technique requires therefore using advanced apparatus, proper sample preparation method and additional correction of experimental data.

The method based on x-ray measurements (SAXS) is equally often used to determine the thickness of lamellar crystals. The diffuse maximum (at SAXS profiles) is converted into well-known long period by applying Bragg's law. If the crystalline volume fraction of the sample is known, the thickness of lamellae can be calculated by using the following relation:

$$L = \psi d \quad (2)$$

where L is the thickness of lamellar crystals, ψ is the crystalline volume fraction (which can be calculated by transforming the mass crystal fraction obtained by DSC into volume fraction by using the relevant densities) and d is the long period.

However, the applicability of the above mentioned x-ray technique to determine the thickness of lamellar crystals is limited to the materials with periodic fluctuation in electron density and hence regular lamellar stacking. SAXS patterns collected for the materials with irregular or defective lamellar structure will lack discrete maxima, the presence of which is indispensable to estimate the value of the long period. Therefore, using SAXS method to determine the thickness of crystals in case of the polymers with impaired lamellar structure would be impossible.

Despite certain limitations, the calorimetric and x-ray methods are most frequently used in determining the thickness or thickness distribution of lamellar crystals of semicrystalline polymers. This paper proved that the applicability of the above mentioned experimental techniques has further limitations. If the amorphous phase of crystallizing polymer is swollen, using the calorimetric or x-ray method to determine the thickness of lamellar crystals may result in obtaining, respectively underestimated or overestimated values. The means for correct analysis will be pointed out. The above effects have been presented on the example of model, miscible, non-cocrystallizing semicrystalline polymer/low molecular weight modifier systems.

2. Experimental

Materials. Polypropylene Moplen HP 456H (PP), MFI = 1,8 g/

10min (at 190 °C, 2.16 kg), by Lyondell Basell was used. High density polyethylene Hostalen GC 7260 (HDPE), MFI = 8 g/10min (at 190 °C, 2.16 kg), by Lyondell Basell was used. Poly(methylene oxide) Tarnoform 300 (POM), MFI = 9.6 g/10min (at 190 °C, 2.16 kg), by Grupa Azoty was used. Polylactide 4032D (PLA), MFI = 19.3 g/10min (at 210 °C, 2.16), by Nature-Works LLC (Minnetonka, MN) was used. Aliphatic-aromatic copolyester (PBASGT) was synthesized in our group. All details of the synthesis procedure were described elsewhere [20]. A nonadecane 99%, by Sigma-Aldrich was used as liquid low molecular weight modifier of polypropylene and polyethylene. A triethyl citrate, (TEC), purity $\geq 98\%$, by Merc KGaA was used as liquid low molecular weight modifier of poly(methylene oxide), polylactide and aliphatic-aromatic copolyester.

Modification. *Modification in the molten state (MS, for polypropylene only).* The process of modification was melt blending using Brabender batch mixer operating at 190 °C for 5 min at 60 rpm. The samples with a following content of nonadecane (wt%) were prepared: 3, 5, 10, 15, 20, 30. The content of modifiers has been verified during supercritical CO₂ extraction. Neat PP was also processed under the same conditions to obtain a reference material. The samples for proper measurements were cut out from 1 mm thick polymer films, obtained by compression moulding and cooled between metal plates. *Modification in solid state (SS).* The process of modification was performed by immersion of polymer samples (obtained by compression moulding and cooled between metal plates) in a modifier bath placed in an oven at 70 °C for 7 days (for polypropylene and polyethylene), 20 days (for poly(methylene oxide)), 34 days (for polylactide) or 14 days (for aliphatic-aromatic copolyester) in order to obtain full penetration of the amorphous phase of the material with a low molecular weight modifier. The content of modifiers has been estimated basing on samples weight increase after completion of the modification process. The reference samples had the same thermal history.

Small-Angle X-ray Scattering (SAXS). The lamellar structure of samples was probed with 2-dimensional small angle X-ray scattering. The Kiessig-type camera with sample detector distance of 1.2 m was coupled to an X-ray CuK α low divergence microsource, operating at 50 kV and 1 mA (GeniX Cu-LD by Xenocs, France). The scattering produced by the sample was recorded with the Pilatus 100 K solid-state area detector of the resolution of $172 \times 172 \mu\text{m}^2$ (Dectris, Switzerland).

Long period was determined from one dimensional sections of 2-D pattern. Background and Lorentz corrections were applied to the curves. Long period was then calculated from position of the maximum of corrected curves using the Braggs law.

Alternatively the long period and thickness of lamellar crystals was determined with the use of correlation function method. All details of this calculation procedure were described elsewhere [21].

Wide-Angle X-ray Scattering (WAXS). Analysis of the crystalline structure of the materials was performed using a computer controlled goniometer coupled to a sealed-tube source of CuK α radiation (Philips), operating at 30 kV and 50 mA. The CuK α line was filtered using electronic filtering and the usual thin Ni filter. The diffraction from crystallographic plane (-113) of PP alpha form was analyzed with the aim of determination of crystallite length in the normal directions to this plane, calculated according to Scherrer formula:

$$L_{hkl} = \frac{0.9\lambda}{\beta \cos\theta} \quad (3)$$

where L_{hkl} is a crystallite length in the direction perpendicular to (hkl) plane, λ is X-ray wavelength, β is the half-width of a diffraction peak, and θ is the Braggs diffraction angle [22]. To determine the half-width of an analyzed peak the deconvolution process of collected profiles was performed using WAXSFit software [23]. The half-widths of a diffraction peaks were corrected for apparatus broadening.

Differential Scanning Calorimetry (DSC). Thermal analysis of the examined materials was conducted using an indium calibrated DSC apparatus (TA Q20). The data was recorded during heating at a

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