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Analysis of Synchrotron WAXD Curves of Semicrystalline Polymers by Means of the *Optifit* Computer Program

Abstract
A new version of the OptiFit computer program intended for the elaboration of large sets of WAXD curves recorded in synchrotron time-resolved experiments is described. The curves are resolved into crystalline peaks and an amorphous halo using a multiobjective optimisation procedure, and a hybrid system which combines a genetic algorithm with a classical optimisation procedure. The program enables a comprehensive analysis of WAXD curves and provides graphic presentation of the results obtained. It is helpful in the quantitative description of time- or temperature-dependent structural transformations taking place in both the crystalline and amorphous phases of the polymers investigated.

Key words: *wide-angle X-ray diffraction, synchrotron, time-resolved experiments, semicrystalline polymers, crystallinity, unit cell dimensions, amorphous halo, genetic algorithm, optimisation methods.*

Introduction

The analysis of wide-angle X-ray diffraction (WAXD) curves of semicrystalline polymers offers information on several important structural parameters related to various levels of the organisation of macromolecules. Apart from the unit cell parameters, it enables the determination of the size of crystallites and the degree of crystallinity. Moreover, in the case of polymers exhibiting polymorphism, the weight fractions of individual crystalline phases can be estimated. The prerequisite for all procedures dedicated to determining of structural data mentioned above by means of the WAXD technique is the possibility of resolving the WAXD patterns into crystalline and amorphous components, i.e. crystalline peaks and an amorphous halo. Most frequently, such a resolution is performed by generating a theoretical function which is fitted to the experimental curve by the least squares refinement. The theoretical function is constructed as a sum of component functions describing crystalline peaks, the amorphous halo and a background. As a result of fitting, all parameters of the component functions are calculated.

At present, the registration time of a single WAXD curve can be reduced to a few seconds or even below one second, thanks to the application of synchrotron X-ray sources of very high brilliance. For this reason, not only static but also dynamic, real-time X-ray diffraction experiments are frequently performed. In such experiments, the transformations of crystalline structure occurring in polymers during thermal treatment can be monitored at high temperature and time resolutions (Figure 1). The total number of diffraction curves registered during these processes can be of the order of 100 or even more, for one sample. This paper presents a new version of the computer program OptiFit [1] which has been designed for elaborating such a large number of WAXD curves. Using the program, one can analyse the whole set of curves registered during a given real-time experiment. As a result, one can determine the dependencies of structural parameters mentioned above on time or temperature. In this way, a comprehensive, quantitative description of investigated processes and transformations is possible.

Description of the OptiFit computer program

In the program, the input data, i.e. intensity (I_e) versus diffraction angle (2q), are transformed into a two-dimensional table, each column of which is related to an individual diffraction curve. Each curve is analysed by the creation of a theoretical function $I_t(x)$, where $x = 2\theta$, best fitted to the experimental one. The theoretical function is composed of functions $F_i(x)$

Equation 1.

$$F_i(x) = f_i H_i \exp\left\{-\ln 2\left[\frac{2(x - x_{oi})}{w_i}\right]^2\right\} + \frac{(1 - f_i)H_i}{1 + [2(x - x_{oi})/w_i]^2} \quad (1)$$

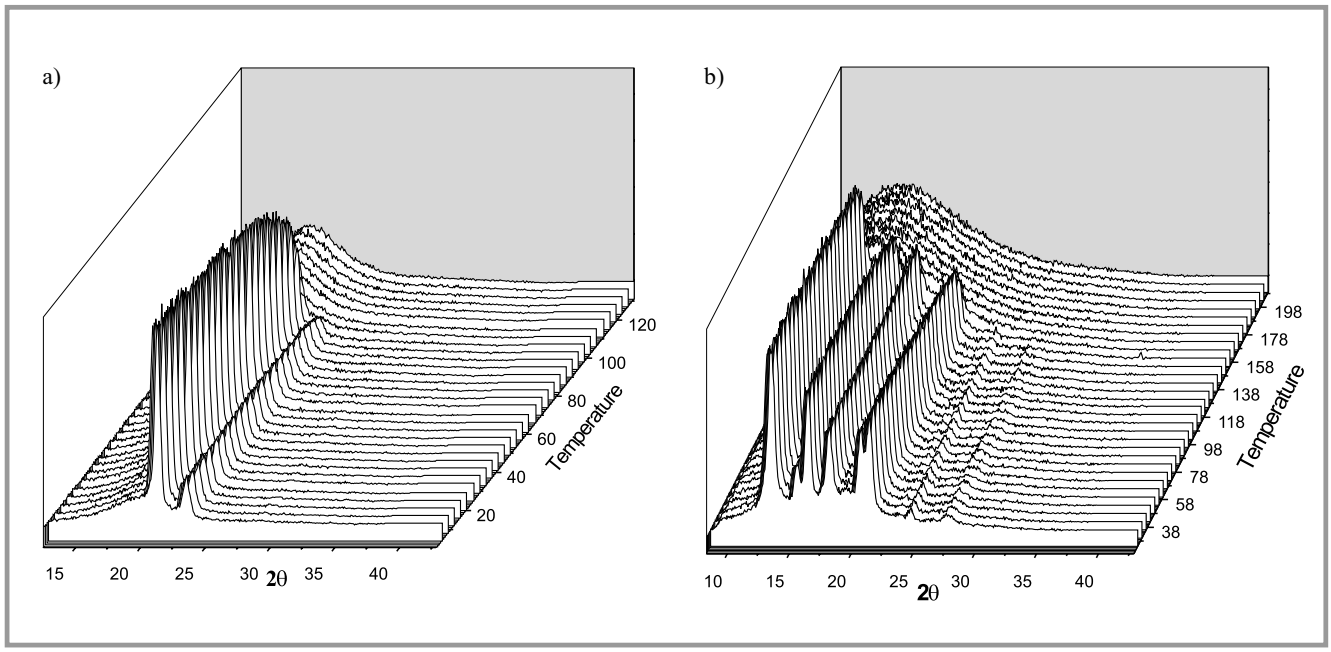

Figure 1. *WAXS patterns of EO copolymer (a) and PP (b), registered during heating from room temperature up to complete melting.*

approximating crystalline peaks, an amorphous halo and a background: (Eq. 1).

The component functions $F_i(x)$ are linear combinations of Gauss and Lorentz profiles, represented by four parameters: peak height H_i, width at half height w_i, peak position x_{oi} and a shape factor f_i which is equal to 1 for the Gauss profile and for the Lorentz one. The background is represented by a third-order polynomial. The total number of unknown parameters of the theoretical function $I_t(x)$ is equal to 4N+4, where N is the number of component functions. Fitting of the theoretical function to the experimental one is performed by using a multiobjective optimisation procedure, i.e. a simultaneous minimisation of the sum of squared deviations between the experimental and theoretical curves, as well as the minimisation of the sum of squared deviations between the experimental curve and the component function representing the amorphous halo. This way of approximating the amorphous halo combines the approaches of Ruland [2] and Vonk [3] and a simple least-squares refinement [4,5]. The method employed makes the resolution more univocal [1,6] and provides a smooth transition from diffraction curves containing crystalline peaks to those related to completely molten sample.

Instead of classical optimisation procedures, such as those devised by Powell [7] or Rosenbrock [8], which are considerably influenced by the choice of the initial parameters, calculations are performed using a hybrid system which combines a genetic algorithm with a classical optimisation method. The main part of the optimisation procedure is accomplished by means of a genetic algorithm. In the genetic algorithm, the set of parameters of a given diffraction curve is considered as a chromosome composed of genes. Each gene represents one parameter. The chromosome is an *n*-dimensional vector of real numbers, i.e. a one-dimensional table of *n* elements. At the first stage of calculations, based on the starting values of the parameters introduced by the user, the program calculates the maximum and minimum values of each parameter. As a result, the ranges of changes in all parameters, and in this way the space of the solutions, are determined. Optimisation starts from a randomly generated population of chromosomes which is drawn from the space of the solutions. Next, a function of fitness is calculated for each chromosome. The fitness function is a weighted sum of two objective functions related to the two optimisation criteria described above. The fitness function permits a comparison of the chromosomes in a given population. The best chromosomes, i.e. those with the highest values of the fitness function, are chosen for 'reproduction'. They are copied and their number is increased in proportion to the value of their fitness function. Next, they are modified by means of crossover operators and mutation operators. In this way, a new generation of chromosomes appears. The crossover operation consists in an exchange of genes between two randomly chosen chromosomes. Mutation consists in the change of a gene in a chromosome assuming some arbitrarily chosen probability of change. This new generation is once again subject to selection and reproduction, as well as to crossover and mutation operators. The process is repeated until the stop condition is reached. The stop condition may be determined by some threshold value of the objective function or an arbitrarily established number of generations. The best chromosome from the last generation represents the final solution, i.e. the set of parameters for which the fitness function has reached the maximum. In a hybrid system, at the end of the calculations a classical optimisation procedure is activated in order to speed up the process.

As a result of fitting, all the parameters of component functions (H_i, w_i, x_{oi} and f_i) are determined. The starting values of the parameters used in resolving the first curve of the analysed set of WAXS patterns are introduced by the user. The program finds the output parameters for this curve using the procedures described above and uses them in the generation of the starting ones for the next curve in the set. As the differences between two neighbouring curves are small, the space of solutions possible for the next curve can be confined, thanks to which the

search time is shorter. When the analysed set of experimental curves is related to melting or non-isothermal crystallisation processes, the calculations should be started from the curve registered at the lowest temperature, because crystalline peaks are best resolved then. For the same reason, in the case of isothermal crystallisation, the calculations should start from the last registered curve.

Based on the determined parameters of the peaks, the degree of crystallinity and sizes of crystallites are calculated for each curve. The degree of crystallinity is calculated as the ratio of the integral intensity under all crystalline peaks to the sum of integral intensities under the crystalline peaks and amorphous halo. The size of crystallites D_{hkl} in the direction perpendicular to the reflecting (hkl) planes is calculated using the Sherrer equation:

$$D_{hkl} = \frac{\lambda}{w\cos\theta} \qquad (2)$$

where λ is the wavelength, w is the width at half height of the peak and q is half of the diffraction angle. The specific data structures used for the storage of calculated parameters provide a three-dimensional graphic presentation of theoretical curves, individual crystalline peaks and an amorphous halo, thanks to which their evolution as a function of time or temperature can be visualised. Additionally, the plots of crystallinity, size of crystals, position and half-height width of crystalline peaks and amorphous halo as a function of time or temperature are available. The plots can be stored as a .wmf file or directly transferred to other Windows applications (MS. Word, Excel etc.)

Experimental

The OptiFit program was used in the analysis of WAXS patterns registered during the melting of an ethylene-1-octene (EO) copolymer (1.77 mol% of 1-octene) and isotactic polypropylene (PP) (Mosten). The samples in the shape of 1mm-thick circles were sealed between thin aluminium foils and heated at the rate of 10°C/min, from 20°C up to complete melting. The temperature of a sample was controlled by a Mettler FP-82HT hot stage.

Time-resolved, wide-angle X-ray diffraction investigations were carried out using the X33 camera of the EMBL (HASYLAB), on the DORIS storage ring of the Deutsches Elektronen Synchrotron. WAXS patterns were registered by means of a position-sensitive linear detector in the range of $8.35^{\circ} \le 2\theta \le 37^{\circ}$. The 2q axis of detector was calibrated with three strong reflections (010), (110) and (100) of the β form of tripalmitine standard [9]. The wavelength of X-rays was 1.5 Å. While heating the samples, diffraction patterns were recorded every 6s, giving the resolution of 1°C for each pattern. Data processing was preceded by normalisation to the intensity of the primary beam and correction for the detector response.

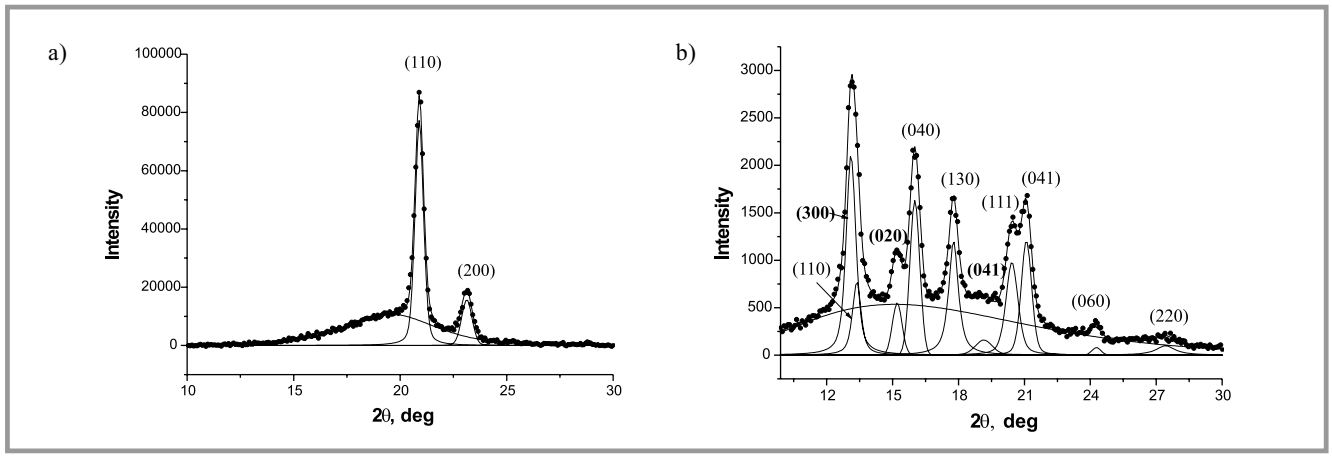

Figure 2. *WAXD curves of EO copolymer (a) and PP (b) resolved into crystalline peaks and amorphous halo. Miller indices of b phase of PP are given in bold type.*

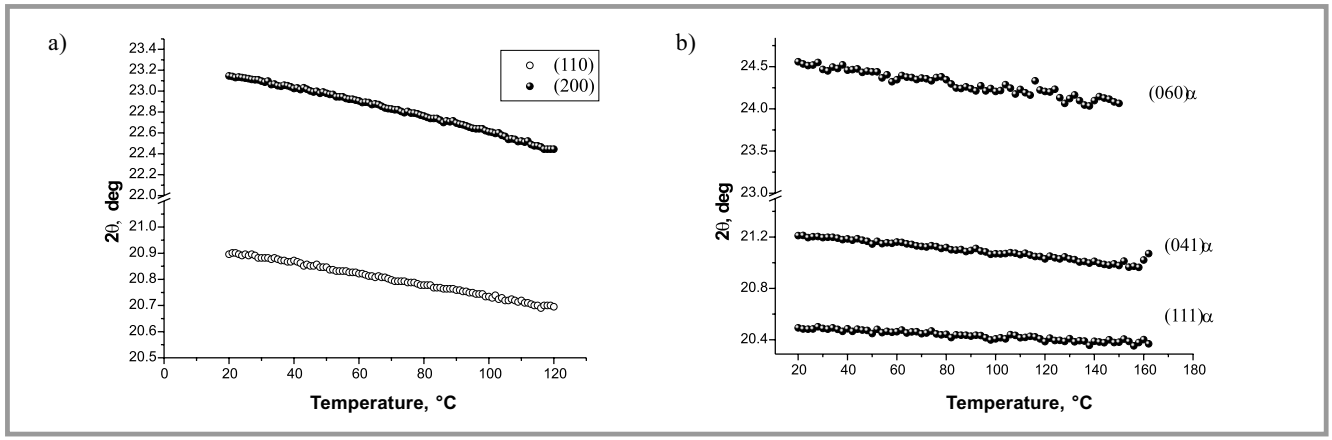

Figure 3. *Positions of crystalline peaks of EO copolymer (a) and PP (b) as functions of temperature during heating.*

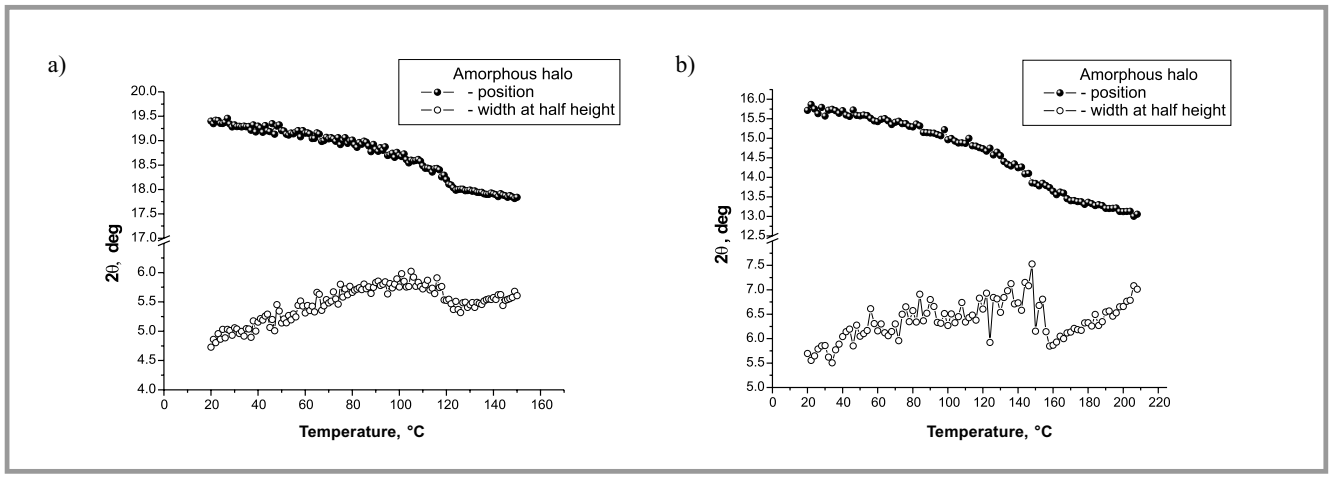

Figure 4. *Position of amorphous halo and its width at half-height versus temperature. (a)- EO copolymer, (b) – PP.*

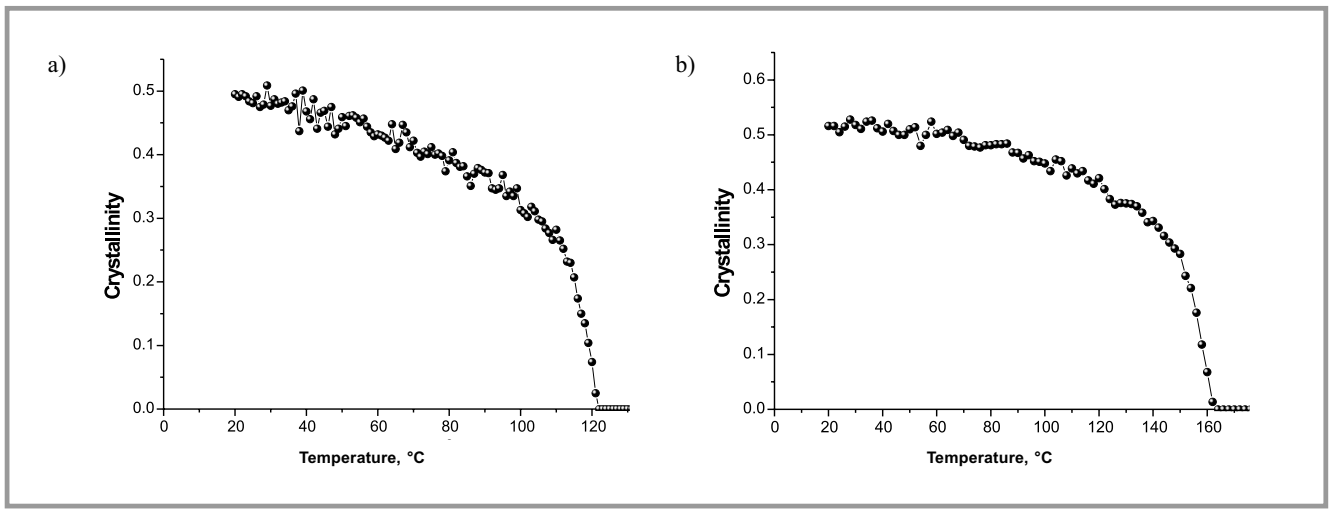

Figure 5. *Crystallinity of EO copolymer (a) and PP (b) versus temperature.*

Results and conclusions

The results of the performed analyses are shown in Figures 2-5.

Example diffraction curves of the polymer investigated, resolved into component peaks and the amorphous halo, are shown in Figure 2. The plots of the positions of crystalline peaks versus temperature are given in Figure 3. The clearly visible, continuous shift in the positions towards smaller angles reflects an increase in the unit cell dimensions caused by thermal expansion. Based on the data presented in this figure, one can calculate the lattice constants, and also trace the changes in the unit cell volume and shape occurring while heating. Such a method was employed in paper [10]. Similarly, Figure 4 presents the changes that occur during heating in the position and width at half-height of the amorphous halo. As the amorphous halo is related to the intermolecular interferences, its position is dependent on the degree of packing of molecules in the amorphous phase and consequently on its density. Hence, by using these plots one can extrapolate information on the changes in the structure of the amorphous phase which are taking place due to thermal treatment. Studies of this type are described in paper [11] published in this issue. Finally, in Figure 5 we see the plots of crystallinity versus temperature.

The presented examples show that the OptiFit computer program is a useful tool for enabling a thorough analysis of WAXS curves recorded during synchrotron time-resolved experiments, providing valuable information on the structural transformation taking place in both the crystalline and amorphous phases of the polymers investigated.

Acknowledgments

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