Application of a multicriterial optimization to the resolution of X-ray diffraction curves of semicrystalline polymers*)

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Abstract: The analysis of wide angle X-ray diffraction (WAXD) curves of semicrystalline polymers is connected with their decomposition into crystalline peaks and amorphous components. To this aim a theoretical curve is constructed which is a best fitted, mathematical model of the experimental one. All parameters of the theoretical curve are found using an optimization procedure. As it has been already proved, a reliable decomposition can be performed only by means of a procedure which effectively performs a multicriterial optimization. It consists in minimization of the sum of squared deviations between the theoretical and experimental curves and simultaneous maximization of the area of the amorphous component. So, the objective function in the optimization procedure is constructed of two criterial functions which represent the two requirements. The proportions between the criterial functions and their significance at different stages of the procedure must be determined by suitable weights. A proper choice of the weights is an important part of the procedure. In this paper a new solution of this problem is presented: the weights are changed dynamically in subsequent steps of the optimization procedure. A few different algorithms of the weights determination are presented and evaluated by means of several statistical method. The optimization procedures equipped with these algorithms are tested using WAXD patterns of popular polymers: Cellulose I, Cellulose II and PET. It is shown that the optimization procedures equipped with the dynamic algorithms of weights determination are much more effective than the procedures using some constant, arbitrarily chosen weights.

Keywords: multicriterial optimization, WAXD method, curve fitting, curve decomposition, statistical verification, statistical test.

Zastosowanie optymalizacji wielokryterialnej do rozkładu rentgenowskich krzywych dyfrakcyjnych polimerów semikrystalicznych

Streszczenie: Dokonanie analizy krzywych dyfrakcyjnych WAXD polimerów semikrystalicznych, związanej z ich dekompozycją na składowe krystaliczne i amorficzne, wymaga zbudowania funkcji stanowiącej matematyczny model zarejestrowanej krzywej dyfrakcyjnej. Do wyznaczenia parametrów tej funkcji stosuje się nieliniową optymalizację wielokryterialną, polegającą na minimalizacji sumy kwadratów odchyleń krzywej teoretycznej od krzywej eksperymentalnej oraz maksymalizacji pola pod składową amorficzną. Funkcja celu jest więc skonstruowana z dwóch funkcji kryterialnych, które reprezentują te dwa warunki. Proporcje między tymi funkcjami i ich znaczenie na poszczególnych etapach procedury optymalizacyjnej muszą być określane przez odpowiednie wagi. Właściwy dobór wag dla funkcji kryterialnych jest jednym z trudniejszych zadań. Zaprezentowano nowe rozwiązanie problemu doboru wag dla funkcji kryterialnych: wagi zmieniano dynamicznie w kolejnych krokach procedury. Zaproponowano kilka różnych algorytmów wyznaczania wag. Algorytmy porównano i oceniono za pomocą testów statystycznych. Procedury wyposażone w te algorytmy zastosowano do rozkładu krzywych dyfrakcyjnych celulozy I, celulozy II i poliestru. Wykazano, że procedury wyposażone w dynamiczne algorytmy wyznaczania wag są znacznie bardziej skuteczne niż procedury wykorzystujące wagi stałe, ustalone arbitralnie.

Słowa kluczowe: optymalizacja wielokryterialna, metoda WAXD, dopasowywanie krzywych, rozkład krzywych, weryfikacja statystyczna, test statystyczny.

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The analysis of the WAXD curves of semicrystalline polymers makes possible determination of such important structural parameters like degree of crystallinity, size of crystallites and weight fractions of polymorphic phases. Moreover, one can trace changes in the positions and shapes of individual crystalline peaks that occur as a result of different physical and/or chemical treatment. Another interesting subject is the influence of various factors on the shape and position of the amorphous halo.

To perform such calculations and analyses, the intensity contribution diffracted by crystalline regions of a polymer has to be isolated in a reliable way from the contribution arising from the amorphous regions [1]. In other words – the WAXD curve has to be decomposed into crystalline peaks and amorphous halo. Most often, such a task is performed using a curve fitting method [2–10]. In this method, an experimental diffraction curve is approximated by a theoretical curve. The last one is described by a function which is a sum of component functions related to individual crystalline peaks, amorphous halos and a background scattering. This theoretical curve is a mathematical model, which should be as close the experimental curve as possible.

Of course, such a relatively simple decomposition of a diffraction curve differs considerably from the well-known Rietveld method [11, 12] as the main aim of the latter one is to refine the crystal structure parameters, not only the peak's profiles. To this aim it uses a feedback between the refined crystal structure parameters from one side and the shapes, positions, and intensities of crystalline reflections on the other side. However, in the case of semicrystalline polymers, the presence of the amorphous phase, as well as very small sizes and considerable distortions of crystallites, cause that in most cases an unambiguous refinement of the crystal structure is not possible.

To construct a mathematical model of an experimental curve we have to know the number of crystalline peaks and amorphous halos present in the curve, their angular positions, heights and widths at half height. These data depend on the type of a polymer and its crystalline structure: crystallographic system and unit cell parameters.

As it has been already proved [13–16], a reliable and effective decomposition of a diffraction curve can be performed only by means of an optimization method which effectively performs a multicriterial optimization procedure.

Generally, a multicriterial optimization involves minimizing and/or maximizing several criterial functions subjected to a set of constraints. In this particular case, it consists in minimization of the sum of squared deviations between the theoretical and experimental curves and simultaneous maximization of the area of the amorphous component in the theoretical curve [16]. So, the objective function in the optimization procedure is constructed of two criterial functions which represent the two conditions. However, these conditions are not equally significant. The first one, *i.e.*, the best fitting of the curves is a superior and dominating requirement while the second criterion fulfills a steering role and helps the optimization procedure to achieve unambiguous solutions. Therefore, the shares of the two criterial functions in the objective function must be represented by suitable weights. A proper choice of the weights is an important part of the procedure. Usually some constant, arbitrarily chosen weights, the same in the whole optimization procedure have been established [17]. In this paper a new approach to this problem is presented: the weights are changed dynamically in the subsequent steps of the procedure. A few different algorithms of the weights determination are described. The effectiveness of the algorithms is compared by means of different statistical methods. The new optimization procedure is tested using WAXD patterns of popular polymers: Cellulose I, Cellulose II and PET.

CONSTRUCTION OF A MODEL

It has to be emphasized that the experimental curve, the model of which is to be constructed must be recorded for a perfectly isotropic sample of the investigated polymer. Otherwise, the intensities and shapes of crystalline peaks may be more or less distorted, depending on the preferred orientation. For this reason, oriented samples like fibers or foils must be thoroughly fragmented and powdered before the measurement. Besides, the curve should be recorded in a 2θ angle range which is wide enough to encompass all crystalline peaks and amorphous halos produced by the sample. It means that in most cases, the curve should be recorded from a few 4–5° up to about 60°.

Starting the construction of the mathematical model of an experimental curve we have to estimate the angular positions of crystalline peaks present in the curve. They can be found by means of Bragg law, knowing the crystallographic data related to investigated polymer, *i.e.*, unit cell parameters and crystallographic system. These positions can also been taken from different data bases like ICCD PDF-4+ [18] if they are available. It should be emphasized that the positions of peaks in the experimental curve may slightly differ from those ones obtained from such calculations. The differences may result from different crystallization conditions, temperature of the polymer sample, *etc.* The shape of peaks can be approximated by various functions: Gauss, Lorentz, Pearson VII, split Pearson, Voight, pseudo-Voight, and a linear combinations of Gauss and Lorentz profiles [4–6, 13, 19–21]. Usually, a diffraction curve contains two broad amorphous maxima (halos). The first maximum is related to the average distance between the polymer chains in the amorphous phase while the second one is related to the average intramolecular C-C distances [6, 13]. They are located at about $2\theta \approx 20°$ and $2\theta \approx 40°$ respectively. Moreover, the model should contain a component representing a background scattering which is stretched out in the whole registration range and generally can be approximated by a third order polynomial.

Summarizing, the theoretical function $\hat{Y}$ is given by equation:

$$\hat{Y} = F(x, \beta_1,..., \beta_k) = B(x, \beta_1,.., \beta_4) + \sum_{j=1}^{N} Q_j(x, \beta_5,..., \beta_k) \quad (1)$$

where: Q_j – a component function (Gauss, Lorentz, Pearson VII, or others) which describes a crystalline peak or amorphous halo, x – the scattering angle 2θ, N –the total number of component functions, B – a third order polynomial approximating background, $\beta = (\beta_1,\ldots, \beta_k)$ – the vector of unknown parameters, k – number of parameters, $\beta \in R^k$ where R^k – a k-dimensional space of solutions.

The experimentally recorded intensity y_i at a given point x_i can be described as:

$$y_i = F(x_i, \beta_1,\ldots, \beta_k) + \varepsilon_i,\ 1 \le i \le n \quad (2)$$

where: n – the number of points in the curve, ε_i – unobserved, random errors.

By means of an optimization procedure, the best estimates $b = (b_1,\ldots, b_k)$ of the unknown parameters $\beta = (\beta_1,\ldots, \beta_k)$ are determined.

Using these estimates, the theoretical intensities:

$$\hat{y}_i = F(x_i, b_1,\ldots, b_k) \quad (3)$$

and the residuals e_i (differences between experimental and theoretical intensities) can be calculated:

$$e_i = y_i - \hat{y}_i \quad (4)$$

As it will be shown in the next paragraph, based on the statistical analysis of the residuals, one can perform verification of the model and assess its quality.

MULTICRITERIAL OPTIMIZATION

Most frequently the objective function in a multicriterial optimization procedure is constructed as a weighted sum of functions representing individual criteria:

$$f = w_1 \cdot f_1 + \ldots + w_i \cdot f_i + \ldots + w_n \cdot f_n \quad (5)$$

where: f_i – a criterial function, w_i – its weight, n – the total number of criteria.

The objective function used in decomposition of the WAXD curves contains two components [16, 17]:

$$f = w_1 \cdot f_1 + w_2 \cdot f_2 = w_1 \cdot S + w_2 \cdot \frac{1}{AAF} \quad (6)$$

where: S – the sum of squared differences between the normalized theoretical and experimental intensities (residuals):

$$S = \sum_{i=1}^{n} (y_i - \hat{y}_i)^2 \quad (7),$$

AAF – amorphous area factor – is the integral intensity *(i.e.*, the total area) of the amorphous component. It should be emphasized that before decomposition, the experimental curve is normalized. It means that the total area of the WAXD pattern (integral intensity) is equal to 1.

The optimization procedure consists in minimization of the objective function. This aim is achieved in successive iterations. In each i-th iteration, a set of parameters is determined for which the objective function reaches its minimal value. Moreover, in each iteration the minimal value of f_1 function (*i.e.*, the minimal sum of squared residuals S_i^{min}) and minimal value of f_2 function (equivalent to the maximum amorphous area factor) are determined.

The roles of the functions f_1 and f_2 are different and their significance changes in the successive stages of the procedure. The first criterion, *i.e.*, the best fitting of a theoretical curve to the experimental one is the superior, dominating and final condition. So, it is particularly important in the last steps of the procedure. The second criterion makes a steering role and gives a direction in which the solution space has to be searched. This is why it is more important at the beginning stages of calculations. This means that the weights w_1 and w_2 of the criterial functions should be changed dynamically during the procedure and their values should be interconnected with the values of the criterial functions. Taking these requirements into account the following seven algorithms with dynamic weights have been proposed. Also an algorithm with fixed weights (algorithm no. 8) has been tested for comparison.

Algorithm 1. Bearing in mind that the total area of the amorphous component is lower than 1 (the experimental curve is normalized to 1 before decomposition) we assume that the weight of the first function is constant and equal to 1 while the weight of the function f_2 is equal to the current value of function f_1 in a given iteration, *i.e.*, to S_i for the current set of parameters:

$$f_i = 1 \cdot f_{1i} + f_{1i} \cdot f_{2i} = S_i + \frac{S_i}{AAF_i} \quad (8)$$

Algorithm 2. In this algorithm the weight of function f_2 in a given iteration is determined by the minimal value of function f_1 in the previous iteration, *i.e.*, S_{i-1}^{min}. Typically the AAF factor ranges from 0.3 to 0.8. For this reason, to make the influence of f_1 and f_2 comparable, we assume that the weight of f_2 is equal to $(S_{i-1}^{min} / 2)$:

$$f_i = 1 \cdot f_{1i} + \frac{S_{i-1}^{min}}{2} \cdot f_{2i} = S_i + \frac{S_{i-1}^{min}}{2 \cdot AAF_i} \quad (9)$$

where: S_{i-1}^{min} – the minimal value of S in the previous iteration.

Algorithm 3. In this algorithm we assume that the weights w_1 and w_2 are equal to the minimal values of function f_2 and f_1 in the previous iteration, respectively:

$$f_i = \left(\frac{1}{AAF_{i-1}^{max}}\right) \cdot f_{1i} + S_{i-1}^{min} \cdot f_{2i} = S_i \cdot \frac{1}{AAF_{i-1}^{max}} + \frac{S_{i-1}^{min}}{AAF_i} \quad (10)$$

where: S_{i-1}^{min} – the minimal value of S in the previous iteration, AAF_{i-1}^{max} – the maximal area of the amorphous component in the previous iteration.

Algorithm 4. The weight of the first function is equal to 1, while the weight of the second function is equal to the ratio of the minimal values of the functions f_1 and f_2 in the previous iteration:

$$f_i = 1 \cdot f_{1i} + \left[S_{i-1}^{min} / \left(\frac{1}{AAF_{i-1}^{max}} \right) \right] \cdot f_{2i} = S_i + \frac{AAF_{i-1}^{max} \cdot S_{i-1}^{min}}{AAF_i} \quad (11)$$

Algorithm 5. Here, the roles of weights w_1 and w_2 are fulfilled by the current values of functions f_2 and f_1 respectively, calculated for a given set of parameters:

$$f_i = f_{1i} \cdot f_{2i} + f_{1i} \cdot f_{2i} = 2 \cdot \frac{S_i}{AAF_i} \quad (12)$$

Algorithm 6. This algorithm is similar to the algorithm 1 but this time the weight w_2 is two times smaller than before:

$$f_i = 1 \cdot f_{1i} + (f_{1i}/2) \cdot f_{2i} = S_i + \frac{S_i}{2 \cdot AAF_i} \quad (13)$$

Algorithm 7. This algorithm is also similar to the algorithm 2 but this time the weight w_2 is two times bigger than before:

$$f_i = 1 \cdot f_{1i} + f_{1i} \cdot f_{2i} = S_i + \frac{S_{i-1}^{min}}{AAF_i} \quad (14)$$

Algorithm 8. In this algorithm the weights are fixed and they do not change in all iterations. From this point of view, it differs considerably from the remaining algorithms. The first weight w_1 is equal to 1 and the second w_2 is equal to the minimal sum of squared residuals calculated in the first iteration:

$$f_i = 1 \cdot f_{1i} + S_1^{min} \cdot f_{2i} = S_i + \frac{S_1^{min}}{AAF_i} \quad (15)$$

To verify which one of these algorithms is more suitable and effective in determination of the most reliable models of experimental WAXD curves, the models obtained with different algorithms have to be carefully compared and tested. To this aim several statistical measures and tests can be used. They are described in the next paragraph.

STATISTICAL VERIFICATION OF A MODEL

In the literature we can found various measures, so-called information criteria, used for the statistical assessment of the quality of models and for their comparison. Comparing several models, the information criteria help to estimate which one of them is most suitable for a given set of experimental data. The best model is the one for which the information criteria reach the smallest values. Some of these criteria are listed below:

1. Integral index S_S [22]:

$$S_S = \frac{1}{n} \sum_{i_p=1}^{n} \left| \frac{\sum_{i=1}^{i_p} \hat{y}_i}{\sum_{j=1}^{n} \hat{y}_j} - \frac{\sum_{i=1}^{i_p} y_i}{\sum_{j=1}^{n} y_j} \right| \quad (16)$$

2. Normalized index S_R [22]:

$$S_R = \frac{1}{n} \sum_{i_p=1}^{n} \left| \frac{\hat{y}_i}{\sum_{j=1}^{n} \hat{y}_j} - \frac{y_i}{\sum_{j=1}^{n} y_j} \right| \quad (17)$$

3. Standard error of estimation of a model S_e [23]:

$$S_e = \sqrt{\frac{\sum_{i=1}^{n} e_i^2}{n-(k+1)}} \quad (18)$$

4. Durbin-Watson statistic d [24]:

$$d = \frac{\sum_{i=2}^{n-1} (e_i - e_{i-1})^2}{\sum_{i=1}^{n-1} e_i^2} \quad (19)$$

5. Sum of squared differences of residuals S [eq. (7)].

In the formulas given above y_i and $\hat{y}_i$ are the experimental and theoretical values respectively, n is the number of points, k is the number of determined parameters and e_i are the residuals, *i.e.*, the differences between experimental and theoretical values: $e_i = y_i - \hat{y}_i$.

The information criteria: S_S, S_R, S_e and S reach zero when theoretical and experimental curves are identical. The lower are their values the better quality of fitting.

The Durbin-Watson d statistic is used to detect serial correlations of the residuals caused by a wrong fit. When the residuals are completely uncorrelated the d statistic amounts to 2.00 [24].

To make the comparison of the models obtained with different algorithms more comprehensive, two other indices have been constructed in this work: a spread index SS_m and effectivity index E. The spread index SS_m is calculated based on the results obtained in 10 successive runs of an optimization procedure equipped with a given algorithm:

$$SS_m = \frac{1}{10} \sum_{i=1}^{10} \frac{S_{mi} - S_{min}}{S_{min}} \quad (20)$$

where: S_{mi} – the sum of squared residuals obtained in the i-th run of an optimization procedure equipped with the m-th algorithm, S_{min} – the minimal sum of squared residuals obtained for all algorithms.

The effectivity index is calculated as the ratio of the sum of squared residuals to the amorphous area factor (AAF), *i.e.*, the area of the amorphous component of a theoretical curve, calculated in the last iteration:

$$E = \frac{\sum_{i=1}^{n} e_i^2}{AAF} \quad (21)$$

Though the informational criteria are useful in comparison and classification of different models they do not allow to decide if the best chosen model is completely reliable and if it can be accepted for further calculations. The only way to estimate credibly the statistical correctness of a model, *i.e.*, the quality of fitting, is to perform suitable tests. The tests must verify if the following conditions related to the residuals are fulfilled:

– residuals are uncorrelated, *i.e.*, there are no hidden trends in their distribution: lack of autocorrelation of the residuals;

– residuals are random, *i.e.*, the experimental points must be randomly dispersed along the theoretical curve;

– residuals are normally distributed;

– residuals are unbiased, *i.e.*, expected value of residuals is zero;

– residuals are symmetric, *i.e.*, the numbers of positive and negative residuals are the same;

– the variance of the residuals must be constant.

The statistical tests used to assess the quality of fitting of theoretical and experimental curves

The statistical tests can help in evaluation of the quality of fitting of the theoretical curve to the experimental one and should answer whether the discrepancies between the curves are significant or not.

Generally, the tests of significance employed in this paper are used to detect if the differences between compared parameters or distribution functions characterizing investigated populations are significant or not. To this aim two types of hypotheses are formulated – a null hypothesis, that the differences between compared parameters or distributions are not significant and the alternative hypothesis which is a contradiction of the null hypothesis and which is assumed in case the null hypothesis is rejected. Verifying the hypotheses one can make two types of errors: error of the first and of the second type. The error of the first type consists in the rejection of a true hypothesis. And in advance assumed probability of the commission of such an error is referred to as a significance level and is denoted as α. The error of the second type is the acceptance of a false hypothesis. In order to verify the null hypothesis, an appropriate test statistic is employed, which is calculated on the basis of the differences between the compared parameters or distributions. If the differences are large (significant), then the value of this test statistic will be enclosed in a so-called critical area, which is dependent on the assumed significance level.

The decision on rejection of the null hypothesis is made basing upon the result of a comparison between the value of the test statistic value and the critical value read out from the test statistic distribution table. Instead, using a relevant software we can calculate the area below the probability density function in the range from the absolute value of the test statistic to $+\infty$. This area is referred to as *p*-value or probability level *p*. The *p*-value is not dependent on the significance level α and is convenient to interpret. If $p > \alpha$, then there is no grounds to reject the null hypothesis. If $p < \alpha$, then null hypothesis is to be rejected in favor of the alternative hypothesis, which means that the difference between the parameters or the distributions is significant. Usually, the significance level α is equal to 0.05.

In this paper the statistical tests are used to investigate if the population of residuals fulfill the conditions listed above. From among many statistical tests such have been chosen which can detect the discrepancies between theoretical and experimental curves related to those conditions and can assess whether they are significant or not. So, the following tests were used:

1. Test of the autocorrelation of residuals.
2. Tests of the randomness of residuals:

– Wald-Wolfowitz series test [23, 25],
– Wilcoxon matched pairs signed-ranks test [23, 25],
– Test of series length [23, 25].

3. Tests of the normality of the residuals' distribution:

– Chi-squared test [25, 26],
– Jarque-Bera (JB) test [25, 27],
– Kolmogorov-Smirnov (KS) test [25].

4. Test of the unbiasedness of residuals [25].
5. Test of the symmetry of residuals [23, 25].

A detailed description of all these tests is presented in the Appendix.

The sixth condition that the residuals should fulfill, *i.e.*, a constant variance of residuals or in other words their homoscedascity means that the residuals should have the same scatter in a whole angular range for which the experimental curve is recorded. In this paper the homoscedascity is checked visually by means of a differential plot representing the residuals value as a function of 2θ angle.

EXPERIMENTAL PART

The optimization procedures with objective functions constructed according to the algorithms described in the paragraph "Multicriterial optimization" were tested using the WAXD curves of isotropic samples of popular polymers: Cellulose I, Cellulose II and poly(ethylene terephthalate) (PET). The curves were recorded in the 2θ range 5–60° with the step size of 0.1° by means of URD-6 Seifert diffractometer using a symmetrical reflection mode and a copper target X-ray tube (λ = 1.54 Å) operated at 40 kV and 30 mA. The CuK_α radiation was monochromized with a graphite monochromizer. Before the calculations a linear background was subtracted from each curve and the curves were normalized in such a way that the total area (integral intensity) under each curve was equal to unity [13]. Decomposition of the WAXD curves was performed by means of a new version of the computer program WAXSFIT, employing the PSO (particle swarm optimization) procedure [16] into which the algorithms 1–8 described earlier are implemented. Starting values for the

angular positions of crystalline peaks used in the optimization procedure were determined based on the unit cell parameters of investigated polymers. All crystalline peaks and amorphous maxima were approximated by a linear combination of Gauss and Cauchy functions.

It should be emphasized that for a given WAXD curve, the optimization procedure equipped with a given algorithm has been run for 10 times. So, for each algorithm 10 results of decomposition, *i.e.*, 10 models were obtained. The final values of parameters (*i.e.*, information criteria) and tests characterizing the algorithm were calculated by averaging the results obtained in those 10 runs.

The models obtained using different algorithms were compared and evaluated by means of various statistical measures, tests and plots. The plots were prepared by means of the program WAXSFIT [13] and Statistica [28, 29].

RESULTS AND DISCUSSION

To compare the algorithms, three aspects were taken into account:

(1) Checking if the conditions that the residuals have to fulfill are met (see paragraph "Statistical verification of a model"). To this aim the statistical tests described in that paragraph were used. The hypotheses were verified with the significance level equal to 0.05. If the result of a given test was positive for a model obtained with a given algorithm, a mark 1 was assigned to this algorithm. If the result was negative, the assigned mark was 0. The final result of this test was obtained as an average of marks obtained in 10 runs.

(2) Evaluation of the quality of fitting of a theoretical model to the experimental curve based on the informational criteria described in earlier paragraph.

(3) Evaluation of the unambiguity and effectivity of the algorithms based on the indices SS_m, E, and on the degree of crystallinity.

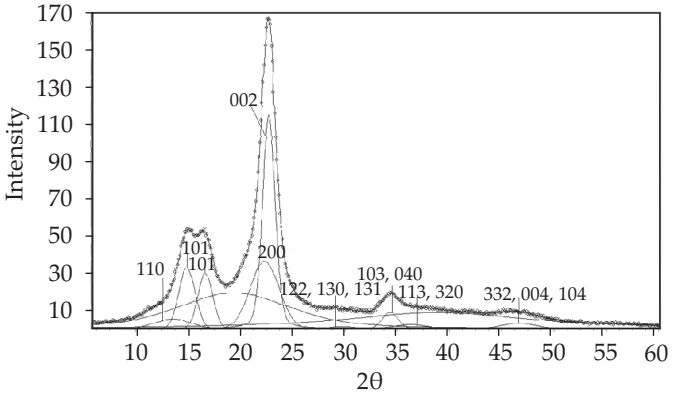

Fig. 1. WAXD curve of Cellulose I: experimental curve – points, the best fitted theoretical curve and its all elements (9 crystalline peaks and 2 amorphous halos) – solid line

Cellulose I

The WAXD curve of Cellulose I and the best fitted theoretical curve are shown in Fig. 1.

The theoretical curve contains nine crystalline peaks and two amorphous maxima. For each component 4 parameters were determined, therefore the total number of optimized parameters was 44. The positions of crystalline peaks determined by the optimization procedure are given in Table 1.

Graphical presentations of the results obtained for the WAXD curve of Cellulose I are given in Figs. 2 and 3. The values of information criteria: S_S, S_R, S_e differ considerably from one another. For this reason they have been standardized before presentation in one plot. To this aim a mean $\bar{x}$ is subtracted from each value of a given variable x_i and obtained result is divided by the standard deviation of this variable:

$$\sigma = \frac{1}{n-1}\sum_{i=1}^{n}(x_i - \bar{x})^2 \qquad \bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i \qquad u_i = \frac{x_i - \bar{x}}{\sigma} \tag{22}$$

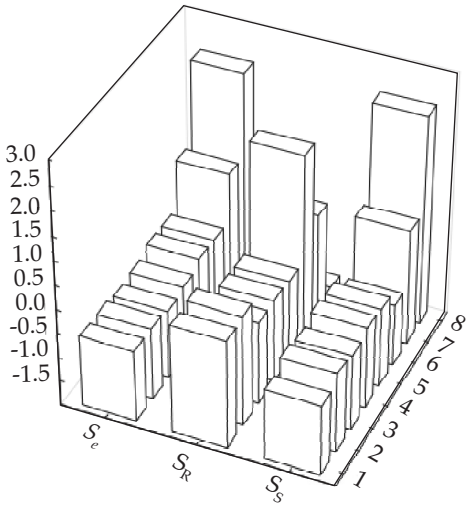

Fig. 2. A comparison of the information criteria obtained for the analyzed algorithms in the case of WAXD curve of Cellulose I; to present them in one plot the criteria were pre-standardized

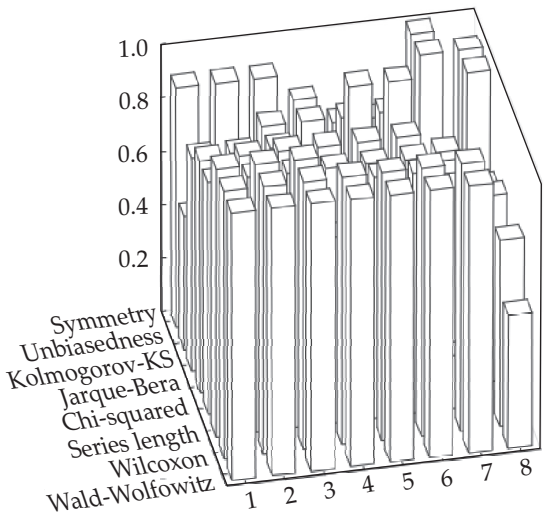

Fig. 3. The results of statistical test for the WAXD curve of Cellulose I