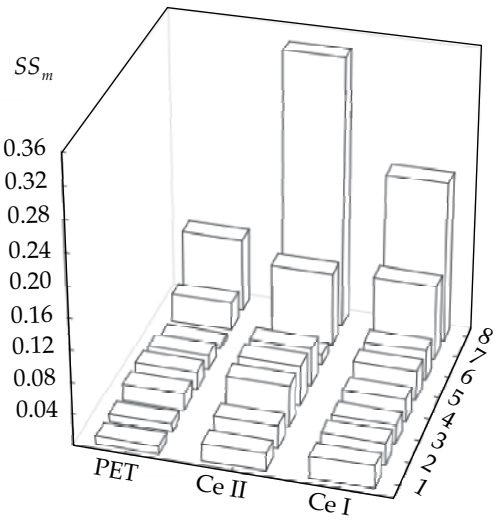

Fig. 15. The spread index SS_m calculated for the tested algorithms according to the formula (20)

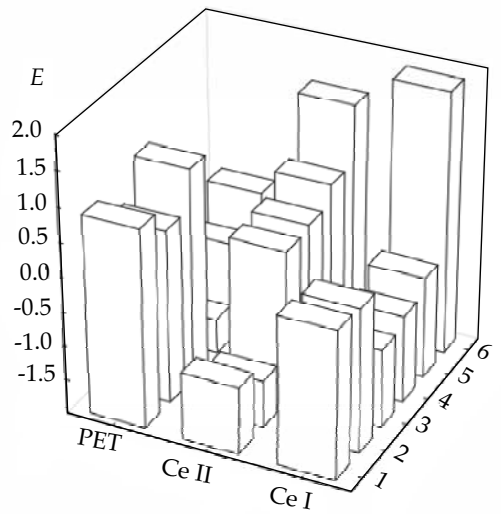

Fig. 16. Standardized effectivity index E calculated for the algorithms 1–6

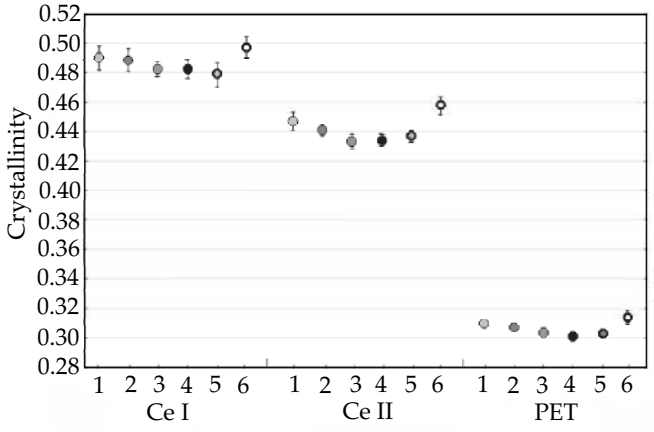

Fig. 17. Degree of crystallinity obtained for investigated polymers with the algorithms 1–6

are not met for these curves. Figure 15 shows the spread index SS_m calculated according to the formula (20). As we can see, also this parameter reaches the biggest, *i.e.*, the worst, values for the algorithm 7 and 8. Performed analysis confirms once again that the algorithms 7 and 8 should not be employed in the optimization procedures.

The effectivity of the remaining six algorithms is compared based on two parameters: first is the effectivity index E [formula (21)] and second is the degree of crystallinity obtained with a given algorithm. As it has been explained in introduction, our aim is to construct such an optimization procedure which leads to a model with the smallest sum of squared residuals and simultaneously maximal area of the amorphous component. This is why the algorithm for which E reaches the lowest value is the best one. Of course the degree of crystallinity and its standard deviation given by such an algorithm should also be the lowest. Figure 16 shows the standardized values of the effectivity index E calculated for the six tested algorithms. In Fig. 17 we can compare the degree of crystallinity obtained for investigated polymers with these algorithms. The degree of crystallinity is averaged over ten runs of an optimization procedure. Standard deviation is also given. We see that for Cellulose I and Cellulose II the index E reaches the highest (*i.e.*, the worst) values for the algorithm number 6. Also the degree of crystallinity obtained with this algorithm reaches the highest values for all investigated polymers. Looking at the formula (13) which defines this algorithm, one can suppose that such results are caused by a too small weight w_2 of the second criterial function f_2.

CONCLUSIONS

The calculations performed in this work show that employing the algorithms from 1 to 6 in the optimization procedures we obtain theoretical curves (models) well fitted to the experimental ones and the requirements related to the residuals, *i.e.*, randomness, normality, symmetry, unbiasedness, and lack of correlation, are fulfilled for these curves. However taking into account the effectivity index E we must state that the algorithm 6 is worse than the remaining ones. Though it provides the quality of fitting (sum of squared residuals in Fig. 12) as good as the first five algorithms, the amorphous area factor is in its case much lower. This means that the weight w_2 of the second criterial function is too low in it. As a result the second requirement of the optimization procedure, *i.e.*, maximization of the area of the amorphous component is not well accomplished. Consequently the degree of crystallinity given by this algorithm is clearly inflated (Fig. 17). On the other hand in the case of the algorithm 7, the weight w_2 is too high and w_1 too low. As a result, the quality of fitting given by this algorithm is noticeably lower (Figs. 2, 6 and 9). So, the algorithms 6 and 7 should be rejected.

However, the worst results are obtained with the algorithm 8 in which the weights w_1 and w_2 are fixed. Their values are chosen in this way that in the first steps of the

optimization procedure, both criterial functions, *i.e.*, the sum of squared residuals f_1 and the inverse of amorphous area factor f_2 have a comparable significance. Nevertheless, after a few dozens of iterations, when the first criterial function f_1 decreases, its meaning becomes lower and lower in comparison with f_2. This is why the quality of fitting obtained with the algorithm 8 is considerably worse as compared with the results provided with the algorithms 1–5 in which the weights are dynamically changed. Thanks to the variability of the weights, the roles of criterial functions f_1 and f_2 in this algorithms can be effectively controlled in the successive stages of the procedure. A detailed comparison and evaluation have shown that the dynamic algorithms 1–5 are equally useful in determination of a credible theoretical model of an experimental curve. The differences between the degree of crystallinity values obtained with these algorithms are very small and do not exceed ± 1.5 %.

The results of this work clearly prove that the optimization procedures equipped with dynamic algorithms of weights determination are very effective tools for a reliable decomposition of the WAXD curves of polymers.

APPENDIX

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

Testing of the autocorrelation of residuals – Durbin-Watson test

Verification of the hypothesis about the lack of autocorrelation of the residuals involves calculation of the Durbin-Watson statistic [23, 24] given by the formula:

$$d = \frac{\sum_{i=2}^{n-1}(e_i - e_{i-1})^2}{\sum_{i=1}^{n-1} e_i^2} \tag{23}$$

where: e_i – the residuals: $e_i = y_i - \hat{y}_i$, n – the number of points.

For high n values ($n > 60$), the Durbin-Watson statistic has an asymptotic normal distribution:

$$N\left(\frac{2(n-1)}{n-m}, \sqrt{\frac{4}{n-m}}\right) \tag{24}$$

where: m – the number of optimized parameters of the investigated model.

Using the value of the test statistic d and the probability density function of the above normal distribution one can calculate the probability level p. Comparing the value of p with the assumed significance level α one can accept or reject the hypothesis about the lack of autocorrelation of the residuals.

The Durbin-Watson statistic has been strongly recommended as providing a quantitative measure of the serial correlations between adjacent points in a diffraction curve.

Testing of the randomness of residuals

The randomness of residuals is the fundamental assumption of the least squares method. Residuals should be alternately positive and negative, *i.e.*, the experimental points should be randomly distributed above and below the theoretical curve. If not, it means that some trends or tendencies in the experimental points layout must occur, which implies that the optimization should be repeated or, that the assumed model should be modified. The randomness of residuals is tested using the series tests and sign tests.

Wald-Wolfowitz series test

In this test [25] to verify the hypothesis about the randomness of residuals, the total number k of series formed of the residuals of the same sign is determined. The higher the number of such series and the shorter they are, the better the fitting of the curves is. If the number of series is low, then long series formed of the residuals of the same sign may occur. It means in turn that at some ranges the curves are not well fitted. For a high number of points, the total number k of series formed of the residuals of the same sign has an asymptotic normal distribution:

$$N\left(\frac{2n_1n_2}{n_1+n_2}, \sqrt{\frac{2n_1n_2(2n_1n_2-n_1-n_2)}{(n_1+n_2)^2(n_1+n_2-1)}}\right) \tag{25}$$

where: n_1, n_2 – the numbers of positive and negative residuals respectively.

On the basis of the determined numbers n_1, n_2, k and the probability density function of the above normal distribution, the probability level p is calculated. If $p > \alpha$, then one can assume, that the residuals have a random nature.

Wilcoxon matched pairs signed-ranks test

The difference between the Wilcoxon test [25] and the previous one is, that it additionally takes into account the values of examined residuals. In the first stage, the residuals are ranked, which means that subsequent numbers are assigned to the absolute values of residuals. In the next step, the established ranks are divided into 2 groups. First group contains the ranks for positive residuals, second group – the ranks for negative residuals. Summation of the ranks within these two groups gives a sum T^+ for positive differences and a sum T^- for negative differences.

Afterwards, the lower of these sums is selected $T = \min\{T^+, T^-\}$. For high n, the T statistic has an asymptotic distribution which is convergent to normal distribution:

$$N\left(\frac{1}{4}n(n+1), \sqrt{\frac{1}{24}n(n+1)(2n+1)}\right) \tag{26}$$

Using the value of T and the probability density function of the above normal distribution, the probability level p can be calculated. If $p > \alpha$, then it is assumed, that residuals are random.

Test of series length

In this test, the length r of the longest series is determined. For a high number of points n ($n\to\infty$), the statistic u has a standard normal distribution N(0,1) [23, 25]:

$$u = \frac{\left(1 - \frac{n}{\mu}\right)\sqrt{\mu^3}}{\sqrt{n \cdot [2^{2r+2} - (2r+1) \cdot 2^{r+1} - 2]}} \quad (27)$$

where $\mu = \frac{1 - 0.5^r}{0.5^{r+1}}$

On the basis of the value of u and the probability density function of the above standard normal distribution, the probability level p is calculated. If $p > \alpha$, then one can assume, that the residuals have a random nature.

Testing of the normality of the residuals distribution

If a theoretical curve is a good approximation of an experimental curve, then the residuals should be normally distributed with the mean equal to zero. A visual way of checking the normality of the residuals distribution is the normal probability plot.

Besides, several tests can be used to examine the normality: chi-squared test for normality and Jarque-Bera [27] test. In most cases, the results of all these tests are in accordance with one another, but even if at least one test confirms that the residuals are normally distributed then the assumption of normality can be considered as met.

Chi-squared test

The chi-squared test [25, 26] requires to group the residuals and divides them into r non-overlapping intervals. The test consists in a comparison of a real number of residuals that fall into each of the intervals with an expected number that results from the assumed normal distribution. To assess the goodness of fit of the experimental distribution of residuals and theoretical normal distributions, a chi-squared statistic is used:

$$\chi^2 = \sum_{i=1}^{r} \frac{(n_i - np_i)^2}{np_i} \quad (28)$$

If the null hypothesis is true, this statistic follows an asymptotic distribution χ^2 with (r-k-1) degrees of freedom, where r is the number of intervals and k is the number of distribution parameters, which have been determined on the basis of the experimental distribution of residuals using the highest credibility method.

There are two such parameters: mean and standard deviation which mean that $k = 2$.

On the basis of the value of the χ^2 statistic and the probability density function of the above asymptotic χ^2 distribution, the probability level p is calculated. If $p > \alpha$, then one can assume, that the residuals are normally distributed.

The Jarque-Bera (JB) test

The skewness coefficient is a measure of the degree of asymmetry of a distribution. It is defined as the third standardized moment of the distribution:

$$A = M_3 / S^3 \quad (29)$$

where: M_3 – the third moment about the mean μ, and S is the standard deviation.

$$M_3 = \frac{1}{n-1}\sum_{i=1}^{n} e_i^3 \quad (30)$$

$$S = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n} e_i^2} \quad (31)$$

Normal distribution is a perfect symmetric distribution. The skewness coefficient for such distribution equals 0. A negative value of the skewness coefficient indicates a negative asymmetry while a positive value of this parameter indicates a positive asymmetry.

Kurtosis is a parameter used to test the slenderness of a distribution. Its value for normal distribution equals 3. The kurtosis of an experimental distribution is determined from the fourth central moment and standard deviation:

$$K = M_4 / S^4 \quad (32)$$

where: $M_4 = \frac{1}{n-1}\sum_{i=1}^{n} e_i^4$ (33)

The JB test [27] is a goodness-of-fit test checking whether the experimental data have the skewness and kurtosis matching these ones of a normal distribution. To verify the hypothesis, a JB statistic is built:

$$JB = \frac{(n-k) \cdot A^2}{6} + \frac{(n-k)(K-3)^2}{24} \quad (34)$$

where: A – skewness coefficient, K – kurtosis, n – number of data, k – number of parameters.

The JB statistic has a chi-squared distribution with 2 degrees of freedom. For the significance level $\alpha = 0.05$, the critical value of JB equals 5.991, which means, that if the JB statistic value is lower than 5.991, then there is no grounds to reject the hypothesis, that this distribution is not normal.

Kolmogorov-Smirnov (KS) test

In the KS test, the quality of fitting of the experimental distribution of residuals and the theoretical normal distributions is measured by means of a statistic, which determines the maximum distance between the experimental cumulative probability function $F_{emp}(x_i)$ and the theoretical cumulative probability function $F(x_i)$ for the normal distribution:

$$D_n = \left(\sqrt{n/2}\right) \cdot \max\left[\left|F(x_i) - F_{emp}(x_i)\right|\right] \quad (35)$$

This statistic follows the Kolmogorov-Smirnov distribution. For the significance level $\alpha = 0.05$, the critical value of the D_n statistic (*i.e.*, the value for which the probability level p is equal to 0.05) amounts to 1.358. If $D_n > 1.358$, then the hypothesis about the distribution normality should be rejected.

Testing of the unbiasedness of residuals

To test the if the residuals are unbiased, a hypothesis, that the residuals expected value of the residuals is equal to zero, is verified. To verify this hypothesis, the following statistic is used [25]:

$$I = \frac{|\bar{e}|\sqrt{n-1}}{S} \tag{36}$$

where: $\bar{e}$– the arithmetic mean of residuals, S – standard deviation of residuals [eq. (18)].

For $n > 30$, the I statistic is convergent to normal distribution. Using the value of I and the probability density function of that normal distribution, the probability level p can be calculated. If $p > \alpha$, then there is no grounds to reject the hypothesis that the residuals are unbiased.

Testing of the symmetry of residuals

The symmetry of residuals means, that the numbers of negative and positive residuals should be the same. The test consists in verifying the hypothesis, that the ratio of the number of positive residuals to the total number of all of them is equal to ½. To verify this hypothesis, a t_{emp} statistic is used [23, 25]:

$$t_{emp} = \frac{\left|\frac{m}{n} - \frac{1}{2}\right|}{\sqrt{\frac{\frac{m}{n}\left(1-\frac{m}{n}\right)}{n-1}}} \tag{37}$$

where: m – the number of positive residuals, n – the total number of data. For $n > 30$, this statistic has a normal distribution with the expected value equal to zero. On the basis of the value of the t_{emp} statistic and the probability density function of that normal distribution, the probability level p is calculated. If $p > \alpha$ one can assume that the residuals are symmetric.

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