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Assessment of the Supermolecular Structure of Standard Polyester Fibres and Those with Reduced Susceptibility to Pilling, as Processed by the Uncontrolled Breaking Method

Abstract

We investigated the supermolecular structure of standard polyester fibres and those with reduced susceptibility to pilling, processed by the uncontrolled breaking method with the use of cable breaking machines. The aim of our investigation was to establish how the structure modification of the PET fibres, which tends towards the reduction of their susceptibility to pilling, influences the fibres' selected physical properties and their supermolecular structure.

Key words: supermolecular structure, polyester fibres, pilling, uncontrolled breaking, structure modification, physical properties.

Introduction

The diversity of the polymers' structural forms means it is impossible to unequivocally, quantitatively define the supermolecular structure's influence on the mechanical characteristics of fibres [1]. The parameters used for structurally describing the supermolecular structure, such as degree of crystallinity, crystallite sizes, thickness of transition zones, crystallite orientation (texture) and macromolecule orientation, degree of lattice imperfection etc., are susceptible to various interpretations in the nature of things.

While considering the possibility of extending polyester cable partition techniques by the uncontrolled tension method, we have evaluated by comparison the sub-

molecular structure of polyester fibres produced at home and abroad; additionally, polyacrylonitrile fibres were also examined. The parameters of the supermolecular structure of fibre types presented in Table 1 were assessed. With the aim of recognising the influence of the supermolecular structure of polyester and polyacrylonitrile fibres on their ability to partition by the uncontrolled breaking method and their physical properties such as the susceptibility to pilling, we carried out the investigations by means of the wide angle X-Ray Scatterings (WAXS) and the small angle X-Ray Scatterings (SAXS) methods. The test were carried out according to the methods described in publications of Hindeleh & Johnson [2], Rosenbrock & Store [3], Aleksander [4] Glatter & Kratky [5], Rabiej & Włochowicz [6], and also Włochowicz & Kwiatkowski [7].

By using the WAXS method, we assessed [4]:

- the degree of crystallinity x_k ,
- the mean size of crystalline zones $D_{(hkl)}$ (by the Scherer formula),

- the azimuth angle of half intensity δ (by the Polanyi method), and
- the orientation ratio of crystalline zones K .

By using the SAXS method, we assessed [5,7]:

- the long period of fibril structure L ,
- the mean thickness of crystalline lamella l_c ,
- the mean quantity of heterogeneity l_p (in relation to PAN fibres), and
- the mean thickness of the transition layer E between crystalline and amorphous zones.

Results of Investigations

Parameters of the supermolecular structure determined by the WAXS method Degree of crystallinity and size of the crystallites

The WAXS diffraction patterns from the samples investigated are shown as dots in Figure 1. The crystalline diffractions and the amorphous component have been separated with a curve-fitting program which

Table 1. Basic characteristics of spinning cables analysed in our investigations (*symbol used by the producer: Silon Company, Czech Republic).

Type of cable	Marking symbol	Type of polymer	Fibre characteristics	Destination after producer	Linear mass of cable, ktex	Linear mass of monofilament in cable, dtex	Trademark	Producer
polyester	WK-2LP	mat	reduced susceptibility to pilling	not defined	50	2.7	Elana	Elana S.A., Poland
polyester	WKN	mat	standard	cutting	50	2.7	Elana	Elana S.A., Poland
polyester	24M	g ^o)	high resistance to pilling	breaking	56	3.0	Tesil	Silon S.A., Czech Republic
polyester	T132	lustre	high strength	breaking	23	1.3	Trevira	Höchst, Germany
polyacrylonitrile	-	-	high resistance to pilling	breaking	96	2.2	Leacryl	Italy

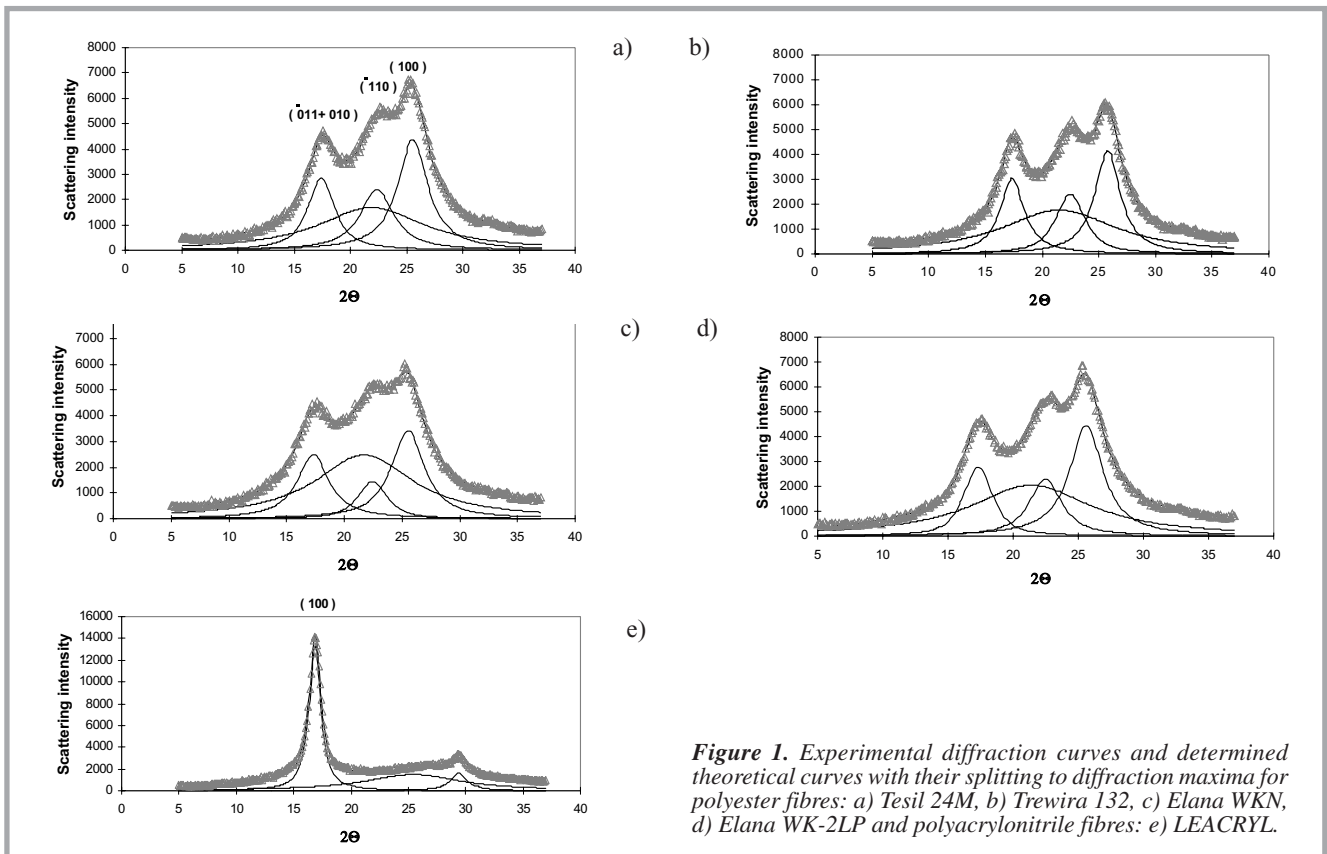


Figure 1. Experimental diffraction curves and determined theoretical curves with their splitting to diffraction maxima for polyester fibres: a) Tesil 24M, b) Trewira 132, c) Elana WKN, d) Elana WK-2LP and polyacrylonitrile fibres: e) LEACRYL.

Table 2. Degree of crystallinity and size of the crystalline zones (*for polyacrylonitrile fibres, the degree of the paracrystallinity was assessed).

Type of polymer	Type of fibres	Degree of crystallinity K	Size of crystalline zones $D_{(100)}$, Å
Polyester	Tesil 24 M	0.655	55.8
	Trewira T 132	0.597	66.2
	Elana WKN	0.522	52.0
	Elana WK-2LP	0.587	58.2
Polyacrylonitrile	Leacryl	0.605*	74.8

Table 3. Orientation ratio obtained from the rectangular fibre diagram.

Type of fibres	Azimuthal angle δ	Directional half-angle ρ	Orientation ratio f_k
	degree	degree	-
Tesil 24 M	22.3	21.7	0.759
Trewira T 132	22.3	21.7	0.759
Elana WKN	22.0	21.4	0.762
Elana WK-2LP	21.7	21.1	0.766
Leacryl	27.3	27.0	0.700

Table 4. Long period, thickness of crystalline lamellae, thickness of transition layer between the crystalline and amorphous zones, determined by SAXS method (L_1 - long period calculated from the scattering curve, L_2 - long period calculated from the correlation function, L - mean value of long period. For the Leacryl sample the mean length of heterogeneity $l_p=85$ [Å]).

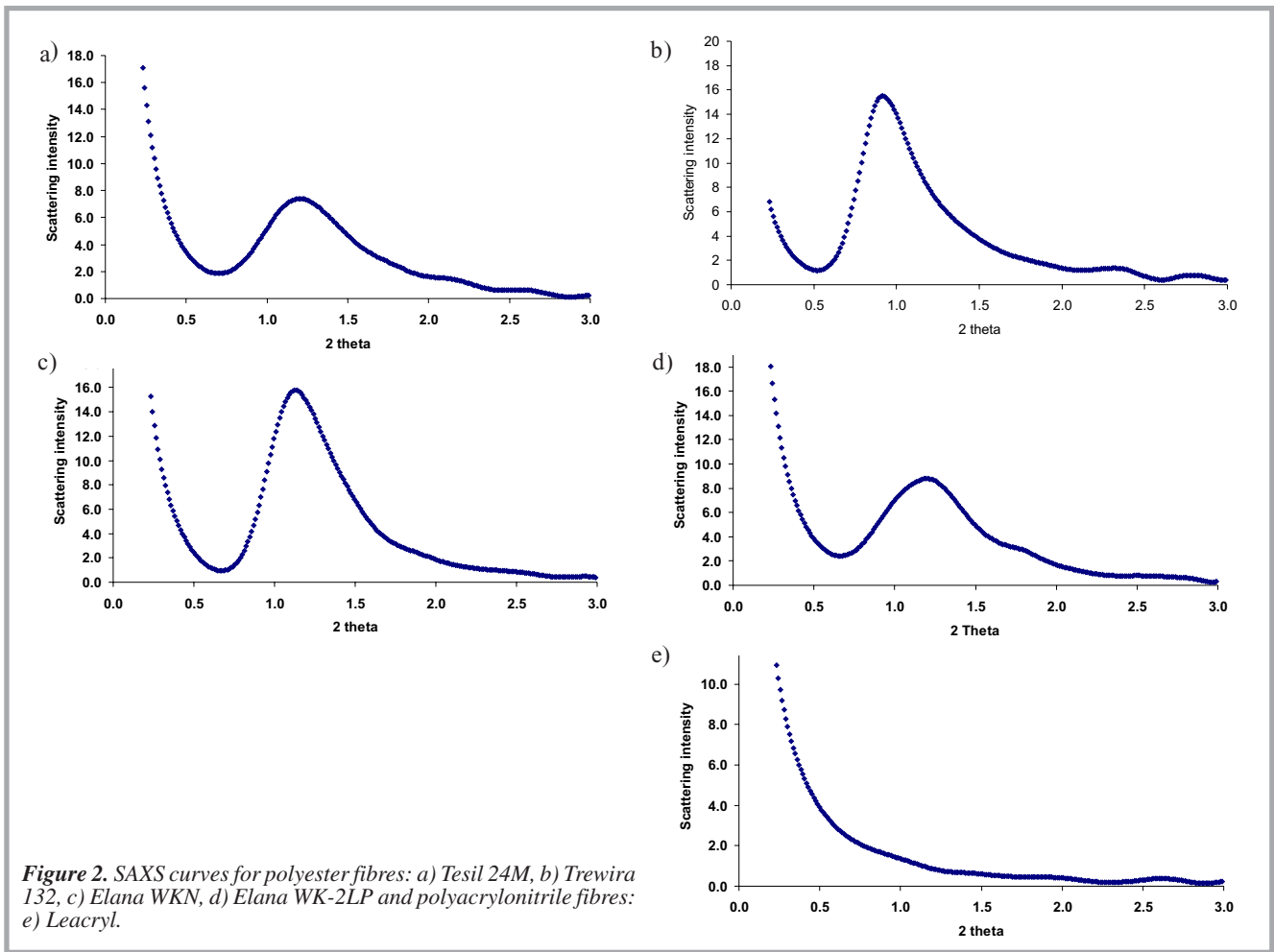
Sort of fibres	Long period, Å			Thickness of crystalline lamellae, Å	Thickness of transition layer, Å
	L_1	L_2	L	l_c	E
Tesil 24 M	64	72	68	43	12
Trewira T 132	88	96	92	54	13
Elana WKN	70	78	74	38	13
Elana WK-2LP	70	72	71	41	11

allows the crystallinity index of the samples and the sizes of crystallites to be estimated. The method described by Hindele & Johnson [2] was used to analyse the WAXS patterns. According to this method, the theoretical curves were obtained by superposition of the curves related to crystalline peaks; one curve is related to the amorphous halo and the other curve is related to the background scattering.

The parameters for adjusting the component curves were determined by a minimisation of the square of the sum of differences between the experimental and theoretical scattering intensities. The minimisations were carried out using Rosenbrock's method [3]. The WAXS deconvolution results are shown as solid lines in Figure 1. The crystallinity index was calculated from the ratio of the integral intensities of crystalline peaks to the total scattering intensity. The mean crystallite sizes were estimated by means of the well-known Scherrer equation. The values of structural crystallinity parameters obtained on the basis of WAXS investigations are presented in Table 2.

Orientation of crystallites

In order to compare the relative degrees of axial orientation in the series of fibres under investigation, the method of azimu-



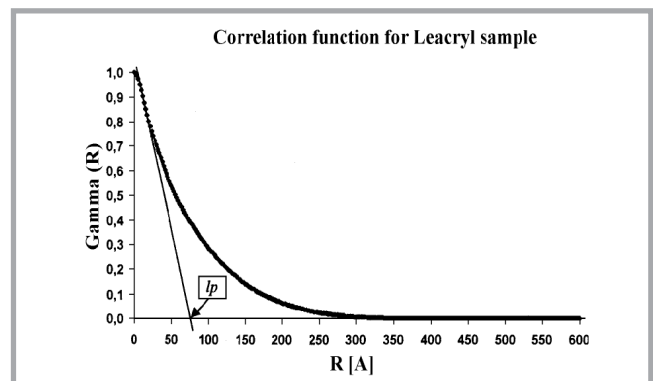
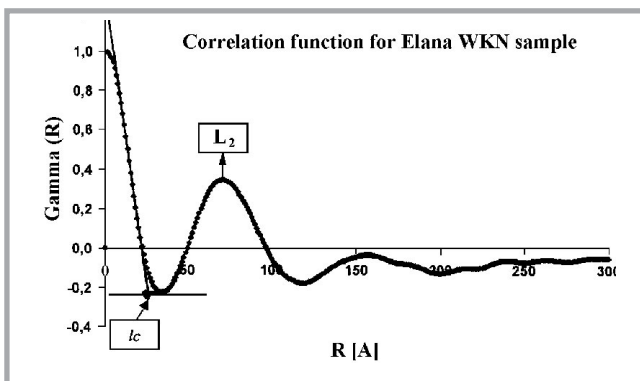
thal width was used. The method is based on measuring the intensity distribution over an azimuthal scan at an appropriate diffraction direction. The measurements were performed for a bundle of fibres with a high degree of parallelism by means of a special device which can be rotated at controlled speed to permit estimation of the azimuthal intensity distribution in a given reflection direction. During the measurements, the fibre axes were perpendicular to the incident X-ray beam. The most common degree-of-orientation indexes are

the azimuthal width at half-maximum intensity (δ), the angle of inclination of the plane normal to the fibre axis (ρ) and the orientation ratio $f_K = (90^\circ - \rho)/90^\circ$. The values of these parameters obtained for the crystallographic planes (100) are presented in Table 3.

Parameters of supermolecular structure determined by the SAXS method

The SAXS curves presented in Figure 2 exhibit a distinct, relatively broad maximum which indicated that a regular fibril

structure is developed in all of the samples investigated. The long period and the thickness of the crystalline layer in the lamellar stacks were also calculated on the basis of SAXS studies. The calculation of the long period was based on the angular position of the maximum visible on the SAXS curve (L_i) and on the position of the first maximum in the correlation function (L_2) derived by the Fourier transform of the SAXS curve. The correlation function was also used for estimation of the thickness of the crystalline lamellae l_c .



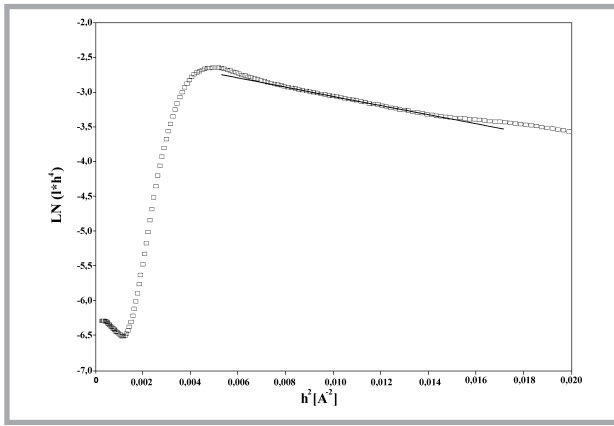


Figure 5. An exemplary Ruland's chart for Trewira T132 polyester fibres.

A typical pattern for this function obtained for Elana WKN polyester fibres is shown in Figure 3. This figure also demonstrates how the values of L_2 and l_c can be estimated on the basis of the correlation function. Figure 4 shows the correlation function for Leacryl polyacrylonitrile fibres whose SAXS curve does not exhibit an interference peak indicating the absence of the fibril structure. For this latter sample, the mean size of electron density heterogeneities lp was also estimated. Figure 5 shows an example of Ruland's plot, which was the basis for determining the thickness of the transition layer between the crystalline and amorphous regions (E) of the samples tested. The values of the parameters obtained by the SAXS method are presented in Table 4.

Result Analysis

Analysis tests aimed at assessing the strength parameters of the polyester and polyacrylonitrile fibres were carried out in order to determine the possible correlations between the supermolecular structure parameters and the strength characteristics of the fibres. The results are shown in Figures 6-10.

An analysis of the results presented in Tables 2-4 and Figures 6-10 allows us to state that the degree of crystallinity K (Table 2) does not significantly influence the tenacity W_t of the fibres (Figure 7), whereas the growth in the degree of crystallinity causes a reduction in breaking elongation E_{r10mm} (Figure 8).

The microfibril morphology along the long period length for polyester fibres is presented in Figure 11, in which the crystalline, mesomorphic and amorphous phases are distinguished. By comparing both types of polyester fibres with reduced susceptibility to pilling, i.e. the Czech TESIL 24M and the Polish WK-2LP, it can

be stated that the thickness of the amorphous interlayer in relation to the lateral dimensions of the fibrils is considerably smaller in the TESIL 24M fibres than in the WK-2LP fibres. Consequently, the flexibility (elasticity) and therefore the fatigue strength of the TESIL 24M fibres is considerably lower than that of the Elana WK-2LP fibres.

Analysing the correlation between the amorphous interlayer and the fatigue bending strength characterised by the number of double bends, we can state that this strength rises in accordance with an exponential function together with the increase in thickness of the amorphous interlayer, as seen in Figure 12. This correlation proceeds with a coefficient of determination $R \approx 0.999$ and a very high computed value of F-Snedecor statistics $F_{comp} = 83.75$ [8]. Other parameters of the

supermolecular structure, such as degree of crystallinity, thickness of crystalline lamellas and their lateral dimensions, do not correspond with the fatigue bending strength of fibres. The only important parameter is the thickness of the amorphous interlayer. This regularity was confirmed for all the types of polyester fibres tested.

The crystallite orientation ratios of all of the polyester fibre samples analysed are very similar and equal $f_K \approx 0.76$ (Table 3). Therefore we cannot evaluate the influence of these ratio changes on the fibre strength characteristics. The Leacryl polyacrylonitrile fibre is characterised by a lower orientation ratio of the order of $f_K \approx 0.70$.

The long period of fibril structure (Table 4) has a higher value for standard polyester fibres than for fibres with reduced susceptibility to pilling. The value of long period for Trewira T132 high strength polyester fibres is especially noteworthy. The very high tenacity of Trewira T132 fibres correlates with this value. Generally, fibres which have higher values of long periods of the fibril structure are characterised by a higher tenacity W_t . This phenomenon is graphically illustrated in Figure 13.

The degree of crystallinity K (Table 2) considerably influences the elongation at break of fibres, independently of the sample length of the tensioned fibres. However, the influence of the orientation degree

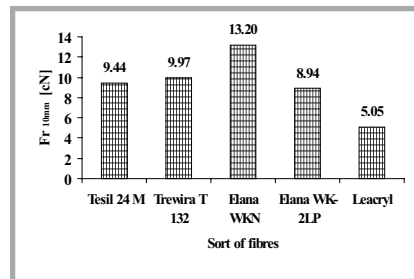


Figure 6. Mean breaking force for 10 mm long fibre segments.

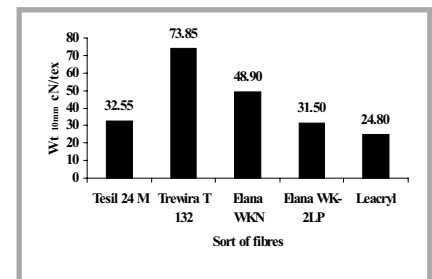


Figure 7. Mean breaking tenacity for 10 mm long fibre segments.

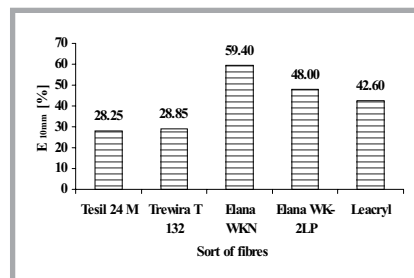


Figure 8. Mean breaking elongation for 10 mm long fibre segments.

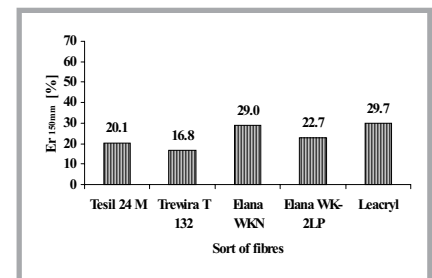


Figure 9. Mean breaking elongation for 150 mm long fibre segments.

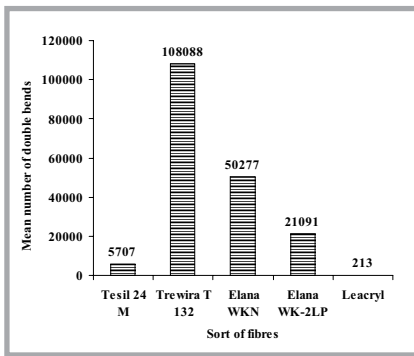


Figure 10. Mean number of double bends.

K on the value of breaking force F_r and consequently on the tenacity W_t is only observed when changes in K cause changes in the orientation of the molecular chains of the fibre material. The main reason for the increase in elongation at break of Elana WKN standard domestic polyester fibres in relation to Elana WK-2LP polyester fibres with reduced susceptibility to pilling is their lower crystallinity.

This can be proved by analysis of a simple (binomial model in series connection) Takayanagi microstructure model [8-11], which makes possible the determination of a factor defining the influence of the change in the sample's degree of crystallinity on the fibre sample elongation at break.

The comparison between values of the mass degree of crystallinity x_m , determined by the WAXS method and values of quotient l_c/L , where: l_c - the thickness of crystallinity lamellas, L - the long period value (SAXS method, Table 4) allows us to accept a simple model of the microfibril structure for all kinds of tested fibres. This model is based on a series configuration of crystallinity lamellas and amorphous interlayers occurring alternately along the microfibril. According to this

model, the ratio l_c/L is the volumetric degree of crystallinity.

Analysing the results presented in Table 5, we can state very small differences between x_m and x_v values. These results confirm both the correctness of the accepted model and the existence of small differences between the mass density of the crystalline and the amorphous phases. The mass and volume degrees of crystallinity can be expressed by the following equations:

$$x_v = \frac{V_c}{V_c + V_a} \quad (1)$$

$$x_m = \frac{V_c}{V_c + \frac{d_a}{d_c} \cdot V_a} \quad (2)$$

where:

V_c, V_a - adequate volume of crystalline and amorphous phases,

d_c, d_a - the corresponding mass density of crystalline and amorphous phases.

For the model in binomial series connection we can state that the relative elongation at break E_r can be expressed by the following equation:

$$E_r \cdot L = E_{rc} \cdot l_c + E_{ra} \cdot (L - l_c) \quad (3)$$

or differently:

$$E_r = E_{rc} \cdot x_v + E_{ra} \cdot (1 - x_v) \quad (4)$$

where:

E_{rc}, E_{ra} - the relative elongation at break for crystalline and amorphous material.

Taking into account that the elasticity modulus of amorphous material for Elana fibres is less than 5% of the elasticity modulus of crystalline material, we can neglect (in the first approximation) the deformability of lamellas during fibre tension, and can make the assumption that:

$$E_r = E_{ra} \cdot (1 - x_v) \quad (5)$$

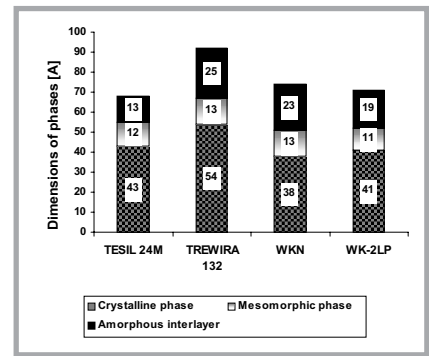


Figure 11. Division of long period of polyester fibres with distinguishing of crystalline, mesomorphic and amorphous phases.

The relative elongation at break E_{ra} depends on both the molecular structure parameters of the polymer and the fibre forming conditions especially such as spinning speed and the degree of technological draft which decided the degree of molecular orientation of the amorphous phases.

For fibres with different degrees of crystallinity ($x_1 \neq x_2$) and an equal degree of molecular orientation in the amorphous phases ($E_{ra1} = E_{ra2}$), equation (3) allows us to write the relation between the relative elongations at break E_{r1} and E_{r2} by the following form [9-12]:

$$\frac{E_{r1}}{E_{r2}} = \frac{1 - x_1}{1 - x_2} \quad (6)$$

The linear mass of monofilaments can be evidence of the similar mechanical parameters of the process of fibre formation. Analysing the data presented in Table 5, we can state that Trewira 132 fibres are characterised by a larger drawing degree, and for this reason they cannot be compared with the remaining fibres in accordance with relation (4). Comparative data for the remaining fibres is presented in Table 6.

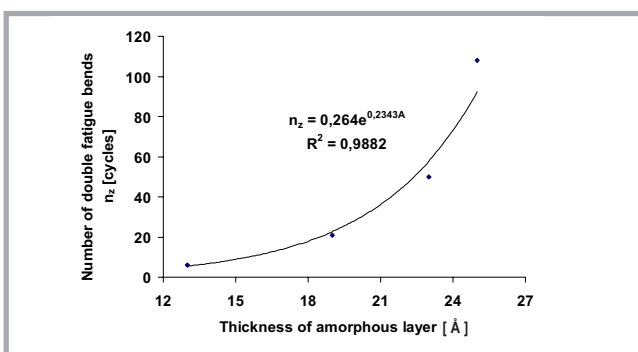


Figure 12. Exponential correlation between bending strength characterised by the number of double bends and the thickness of amorphous layer.

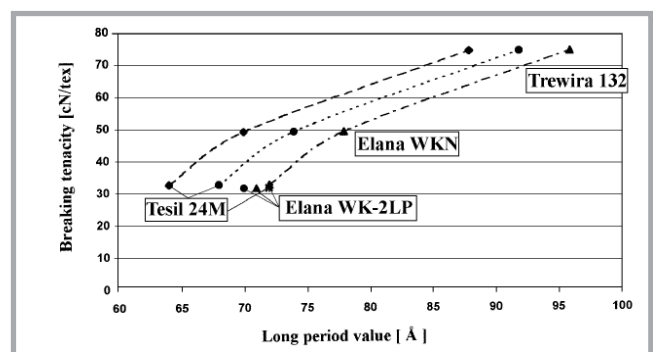


Figure 13. Correlation between tenacity and the value of long period. Designations: L - \blacklozenge , L_1 - \bullet , L_2 - \blacktriangle .

Table 5. Degree of crystallinity and x_v .

Type of fibres	Linear mass of monofilament, dtex	x_m	x_v
Tesil 24 M	3.0	0.655	0.632
Trewira T 132	1.3	0.597	0.587
Elana WKN	2.7	0.522	0.514
Elana WK-2LP	2.7	0.587	0.577

Table 6. Comparative results for the remaining polyester fibres. Designations: factor

$$A = \frac{1-x_1}{1-x_2}, \Delta - \text{error caused by factor A [\%]}.$$

Type of fibres	A	$(E_{r1}/E_{r2})_{10}$	Δ_{10} , %	$(E_{r1}/E_{r2})_{150}$	Δ_{150} , %
Elana WKN/ Elana WK-2LP	1.157	1.237	6.5	1.277	9.4
Elana WKN/ Tesil 24 M	1.391	2.103	34	1.443	3.6
Elana WK-2LP/ Tesil 24 M	1.197	1.699	29.5	1.129	6.0

The results received for fibres of 150 mm measuring length are satisfactory because the differences between the empirical and theoretical (model) values are similar to the coefficient of variation calculated for mean values E_r . In the case of fibres of 10 mm measuring length, the results are not satisfactory because the measurements of fibre elongation are distorted by a significant apparatus measuring error caused during the breaking test by the extrusion of fibre material outside the pneumatic jaws. This effect is proportional to elongation at break, and is most significant for Elana WKN and Elana WK-2LP fibre types. For example, the outflow of a fibre segment of about 0.5 mm from each jaw influences the increase in the measuring results by a relative elongation of about 10%. In the case of testing fibres with 150 mm measuring length, the effect described is not so significant, and nor can any influence on the measurements of breaking force be stated.

This information is very important from the point of view of the technological process of partition by the breaking or cutting method with the use of cable breaking machines or converters. It should be emphasised that the partition process of the cable is carried out in order to achieve fibres of worsted spinning length, i.e. fibres of lengths around 150 mm.

The differences observed between the results calculated from equations (4) and (5) and determined by equation (2) do not affect the correctness and usefulness of equations (1) to (4). On the other hand, they indicate the various degrees of orientation of the amorphous zones compared of the fibres. It is generally known [12] that the increase in general orientation significantly decreases the elongation at break.

Because the effectiveness of man-made fibre cable partition at stapling fibres by the method of uncontrolled breaking depends on the relationship between the breaking force and the elongation at break, the most essential parameters of the supermolecular structure of fibre material in this process are the value of long period, the degree of crystallinity and the general orientation of the polymer.

Conclusions

- The supermolecular structure parameters, such as degree of crystallinity, thickness of crystalline lamellas and their lateral dimensions do not have a major influence on the fibres' fatigue bending strength. The only important parameter is the thickness of the amorphous interlayer.
- The influence of degree of crystallinity on the value of the fibre's breaking force and consequently on the tenacity value is only observed when changes in this degree do not cause any change in the molecular orientation of the chains in the fibre material.
- Tenacity increases together with the growth in the value of long period. This means that in fibres characterised by a large value of long period, lamellae with a small number of structural defects and a high degree of molecular orientation in amorphous zones are formed. A decrease in local tension concentration is a consequence of this phenomenon.
- Besides the crystallite orientation ratio, the degree of crystallinity also significantly influences the elongation at break of fibres.
- Knowing the value of elongation at break of a given fibre and the factor A defined by equation (1), one can forecast the elongation at break of a se-

cond fibre with an optional degree of crystallinity.

- The supermolecular structure parameters obtained in connection with the level of elongation at break and its correlation with strength do not allow final decisions to be made about the suitability or unserviceability of a cable of polyester fibres with reduced susceptibility to pilling of the Elana WK-2LP type and a cable of Elana WKN standard polyester fibres for their partition to staple fibres by the method of uncontrolled breaking. However, it can be indisputably stated that fibres with a higher general orientation ratio and degree of crystallinity should ensure random breaking of fibres.



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