THE INFLUENCE OF ACID DYES UPON SOME STRUCTURAL AND PHYSICO-MECHANICAL INDICES OF POLYAMIDE FIBRES

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Abstract

The influence of three acid dyes upon some physico-mechanical indices of polyamide multifilament yarn has been studied as a consequence of the structure modifications which occur during the dyeing process. It has been established that, irrespective of the differences in the chemical composition of the dyes, the modifications in the properties of the samples used are quite similar. Some structural characteristics, tenacity and elongation at break, crease resistance and the critical time of dissolution, have been determined. The dependencies of the indices listed on the dye concentration are of a complex character, which reflects the gradual penetration of the dye molecules into the inter-fibrillar and intra-fibrillar amorphous areas of the structure which are different in solidity. The fluctuations in the course of the dependencies in the area of the lowest concentrations are the result of the combined influence of the processes of improvement of the crystal phase and the relaxation phenomena, occurring in the most accessible amorphous areas of the fibrous structure. With the increase in the dye concentration, the so-called 'cross-linking effect' starts to appear, as a result of the formation of inter-molecular links of the polymer-dye-polymer type, which influence the properties under investigation in a characteristic way. The increase in the dye presence in the substrate provokes the repeated alternation of the above-mentioned phenomena in the thicker amorphous areas of the samples, with a pronounced influence of the 'cross-linking effect' in the highest concentrations.

Key words:

polyamide multifilament yarn, dyeing, acid dyes, modification, supra-molecular structure, relationship, physico-mechanical indices

Introduction

Dyeing involves dye penetration into the fibre mass and its fixation by certain known mechanisms. This maximally simplified definition does not however give a clear idea of the complexity of the number of physical, physico-mechanical and chemical phenomena which occur during the dyeing process.

First of all, during the dyeing process, conditions are created for liberating the segmental mobility of the polymer molecules, in this case the polyamide molecules. It is a necessary condition for the penetration of the dye particles into the net of macromolecules which make up the amorphous areas of the fibres. Therefore dyeing is generally carried out at comparatively high temperatures, in the presence of substances which cause the swelling or at least the plasticising of the polyamide. Water is a universal medium, causing the swelling and plasticising not only of the polyamide. It is also a suitable carrier of the dye molecules.

When dyeing with acid dyes, the dye bath is slightly acidic and facilitates the swelling of the substrate. When temperatures of the dyeing process are higher than T_g (the glass transition temperature), a sharply increased mobility of the molecule segments is observed in the polymer. That is why dyeing is effected within the temperature range of 45-98°C, when the polyamide under these conditions is above its glass-transition temperature and is in a highly elastic state [1, 2].

It is well known that this is the state where the segmental mobility of the macromolecules in the amorphous areas evinces all its special features, the most evident of which is the rapid diffusion of
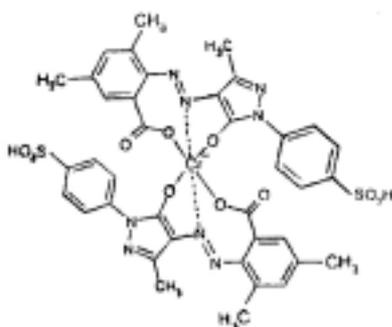
dyes. However, this mobility is a prerequisite of a number of concurrent phenomena, which can be summed up in oneexpression – the relaxation of the supra-molecular structure.
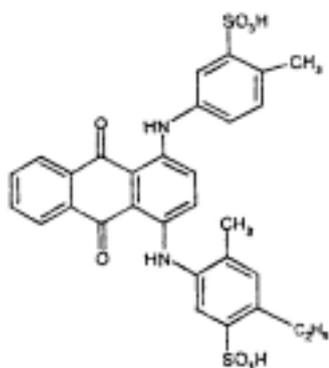
Erionyl rubin 5-BLF (CIBA) – 1
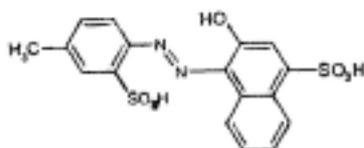
Acidol orange 3RL (BASF) – 2

Acidol brilantgelb M-3GL (BASF) – 3

Figure 1. Chemical structure of the acid dyes used

Taking into consideration the molecular-kinetic nature of the relaxation, it can be expected that in the presence of active low-molecular particles such as acid dyes, the activating energy of the transformation processes of the polymer structure will decrease depending on their concentration [2–4]. Consequently, the concentration of the acid dyes should be one of the determining factors for the direction and extent of the processes of structural transformation in the substrate during the dyeing process.

Another essential factor, to which little attention is paid, is that after the end of the dyeing process, the molecules of the acid dyes remain tightly fixed in the amorphous areas of the substrate, which are responsible to a high extent for the deformation behaviour of the polymer [5–8]. This is due to the chemical structure of the dye particles with their intrinsic poly-functionality, allowing the formation not only of chemical bonds, but also of contacts, arising on the basis of the van der Waals interactions and additional hydrogen bonds, which are different in character [1, 9].

The concentration of the acid dyes in respect to the textile material varies within wide limits, but it generally is from 0.05 to 5%. Such an amount of the substance with its own definite volume, included in the mass of any polymer product, should appreciably influence the relaxation processes of the structure, with a natural effect upon the physico-mechanical properties of the samples.

The interrelation between the presence of acid dyes in the polyamide substrate and the modifications in the supra-molecular structure of the polymer has been studied by other authors as well [10–12], but no investigations have been made on the influence of the dye concentration upon the course of these processes and the effect upon the physico-mechanical indices of the dyed samples.

The influence of the concentration of three acid dyes upon certain structural and physico-mechanical indices of polyamide multifilament yarn and woven fabric is studied in the present work.

Experimental

Materials Used

The investigations were carried out with:
- **polyamide multifilament yarn PA MFY 8 tex** ('Vidlon' from Vidin, Bulgaria) with the following characteristics: PA6 MFY 8.42 tex f 32 Z 310 (BDS 17281–92); deviation from linear density 1.3% (BDS EN ISO 2060-99); linear density after doubling 8.48 tex; doubling coefficient 30; angle of doubling (β) 7°; contracting after doubling 0.6%; yarn diameter 0.142 mm with deviation from the diameter 1.1% (BDS EN ISO 2061-99);
- **polyamide woven fabric with plain weave** ('Filatex' from Kazanlŭk, Bulgaria); area mass 67.7 g.m^{-2} (BDS EN 12127-00); density of cloth (sett): 35 warp yarn/cm × 35 weft yarn/cm (BDS EN 1049-2–02); woven from polyamide multifilament yarns with the following characteristics:
- **polyamide warp yarn** PA WARP Y 8.42 tex f 32 Z 230 (BDS 17281–92); deviation from linear density 1.1% (BDS EN ISO 2060-99); linear density after doubling 8.46 tex; doubling coefficient 27; angle of doubling (β) 6°; yarn contracting after doubling 0.5%; yarn diameter 0.147 mm with deviation from the diameter 1.5% (BDS EN ISO 2061-99);
- **polyamide weft yarn** PA WEFT Y 8.42 tex f 32 Z 150 (BDS 17281–92); deviation from linear density 0.8% (BDS EN ISO 2060-99); linear density after doubling 8.33 tex; coefficient of doubling

14; angle of doubling (β) 3°; contracting of the weft yarn after doubling 0.1%; yarn diameter 0.133 mm with deviation from the diameter 0.9% (BDS EN ISO 2061–99).

Dyeing was carried out with the following three acid dyes: Erionyl rubin 5-BLF (CIBA), Acidol orange 3 RL (BASF) and Acidol brillantgelb M-3GL (BASF), in the concentration range of 0.0 to 5.0%. For brevity in some of the figures and tables, the dyes are designated with the numbers indicated in Figure 1. In accordance with the specifics of the analyses conducted, the test samples have been prepared from polyamide multifilament yarn PA MFY 8 tex and polyamide woven fabric (PAWF), dyed in the above-mentioned concentrations.

The dyeing was conducted on an Ahiba Polymat (AHIBA AG) laboratory dyeing apparatus under the following conditions: the wetted textile material was dipped into a dye bath with a module M of 1:100, containing x% dye and 20% (in relation to the mass of the material) NaCl at an initial temperature of 40°C. After a 10-minute treatment under the above-mentioned conditions, 2% (in relation to the mass of the material) of 30%-water solution of CH_3COOH (pH 4.5 – 5.5) is added to the bath, and after a 5-minute treatment, the bath temperature was increased at the rate of 6°/min until boiling point (98°C). Dyeing continued for 40 minutes at boiling point. Then the bath was cooled down to 60°C and the the dyed samples were washed in warm and cold water.

The degree of extracting the dye has been determined by colorimetry of the residual dye baths on a SPECOL spectrophotometer (Carl Zeiss Jena) and compared with previously prepared standard absorption curves for the respective dyes. The real dye concentration in the substrate has been obtained by a correlation coefficient corresponding to the estimated percentage of the extracted dye.

Methods Used

Wide-angle X-ray scattering (WAXS) has been conducted on a TUR M62 apparatus (Carl Zeiss Jena) from fixed samples of equal mass and a mobile counter with the following working characteristics: CuK_α-radiation (λ = 1.542Å); I_a = 20mA, U_a = 35 kV; angle speed of the goniometer of 1°/min; Ni-filter; constant registration in the area of 2Θ 3-30° [13, 14].

The X-ray degree of crystallinity (α^{waxs}) has been determined according to the following formula:

$$\alpha^{waxs} = [\, I_{cr} / I_{cr} + I_{am}] * 100 \, [\%],$$

where:

I_{cr}–intensity of the crystal reflexes;
$I_{cr} + I_{am}$–total area of the diffractogram.

The dimensions of the crystallites have been determined from the diffractograms for reflexes 002 (Θ = 11.5–12°) and 100 (Θ = 10.5–11°) according to Sherer's method [13].

The DSC analyses have been conducted on the Perkin Elmer DSC 2C apparatus, calibrated with **In** according to the instructions for use for the apparatus, in a heating regime from 350 K to 600 K, at a constant rate of heating of 20 K/min in an argon atmosphere.

The degree of crystallinity (α^{DSC}) [14] is determined according to the following formula:

$$\alpha^{DSC} = (\Delta H / \Delta H°) * 100 \, [\%],$$

where:

$\Delta H°$- melting of temperature 100% crystal polymer [15].

The birefringence (Δn) was determined with an Ernst Leitz Wetzlar polarisation microscope equipped with a Berek calcite compensator [16–19]. The single filaments of the dyed samples have been prepared with Canadian balsam. The results presented are the average value of 10 measurements for each concentration.

Δn has been determined according to the formula:

$$\Delta n = R / d, \text{ where}$$

where:

R–difference in the run of the waves, which are obtained when the light rays pass through the yarn;
d–yarn diameter.

$$R = C * f(i),$$

where:

C–a previously calculated constant, specific for each compensator;

f(i)–a function of compensation expressing the dependence of the difference in the run of the waves on the angle of rotation of the compensator (i). f(i) is constant for each compensator from the Berek type; its values, calculated in advance, are attached to the compensator in the form of tables.

The angle of rotation of the compensator (i) is determined according to the formula

$$i = [\sum_{i=1}^{n} a_i / n + \sum_{i=1}^{n} b_i / n] / 2, \ n = 10$$

where:

a_i–angle of rotation of the compensator in one direction from the position of maximum illumination of the yarn in opposite parallelism to the object and the compensator (decreasing the interfering colours) up to complete compensation for the difference in the run of the waves, which corresponds to the total matting of the yarn;

b_i–angle of rotation of the compensator in the opposite direction up to the total matting of the yarn, i.e. up to full compensation for the difference in the run of the waves.

The tenacity and elongation at break have been determined on a WPM apparatus (Werkstoffprüfmaschinen, Leipzig) with an inter-jaw distance of 0.5 m and a stretching rate of 0.2 m/min, maintaining a constant speed of movement of the jaws.

The measurements were conducted with non-dyed and respectively dyed polyamide multifilament yarn PA MFY 8 tex, conditioned in advance for 24 hours under standard climatic conditions.

The data presented in Figures 8 and 9 are the average value of 20 measurements for each concentration of the three dyes (BDS 9894–83) – v – values between 0.6% and 2.47%..

The crease resistance (BDS 9589–89) of the samples has been determined as the ***angle of restoration after creasing (ARAC)*** of samples with dimensions 2 × 4 cm, cut longitudinally along the warp and weft yarns from PA fabric (PAWF). The samples are folded perpendicularly to the above-mentioned fibres, and then loaded with a weight of 1 kg for 30 minutes. After removing the weight, the samples are left to relax for 30 minutes, and the angle between the two folded parts is measured. The ARAC is determined according to the following formula:

$$ARAC_i = [\sum_{i=1}^{n} ARAC_{warp} / n + \sum_{i=1}^{n} ARAC_{weft} / n] / 2,$$

where:

$ARAC_i$ is the average angle for a definite concentration;

n = 20 experiments conducted under standard climatic conditions (v – values between 0.91% and 2.31%).

The critical time of dissolution was established according to Schwertassek's method [20]. The time necessary for the dissolution of individual elementary fibres of the polyamide multifilament yarn PA MFY 8 tex in a 65% solution of H_2SO_4 under a load of 0.3 g at a temperature of 20°C was measured. The values in Figure 11 are the average of 20 measurements of each separate concentration (v – values between 1.09% and 3.40%).

Results and Discussion

Structural modification of PA samples under the influence of the acid dyes concentration

It is known that **the intensity of the wide-angle diffraction of X-rays** is related to the modification in the phase composition of the samples. The WAXS experiments show that the dyed samples, irrespective of the dye used and its concentration, have characteristic peaks for α–modification (between θ = 9.5–10° and θ = 11.5–12°) and for γ–modification (θ = 10.5–11°) [21–23].

It should be stressed that a clearly expressed reflex (100) is observed for all concentrations of the three dyes, connected with the presence of the hexagonal crystal modification. Although the intensity of this reflex is not predominant over reflex (002) of the monoclinic shape, the equal participation of the γ–modification in the crystal structure of the samples is evident.

Another characteristic feature is the comparatively low intensity of reflex (200) which, although it increases considerably in the dyed samples in comparison with the untreated polyamide

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multifilament yarn, remains less clearly expressed than towards reflex (002) (Figure 2). This is a kind of indication that the monoclinic areas in the crystal structure are rather far from perfection.
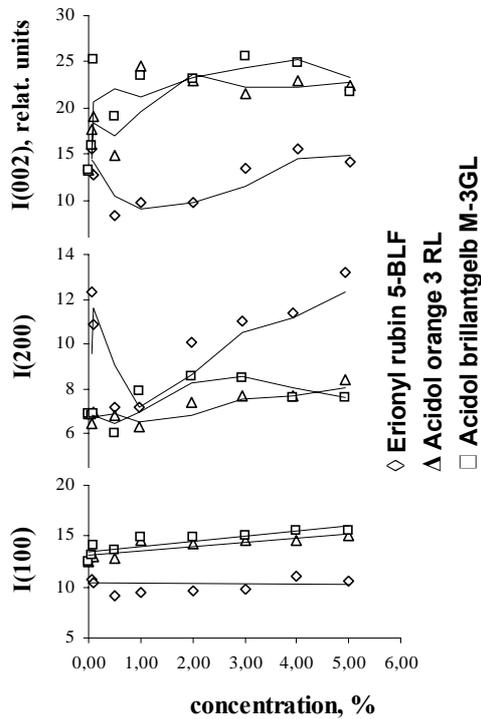

Figure 2. Modification in the intensity of reflexes (002), (200) and (100) depending on the concentration of the dyes used

With the increase in the concentration of the three dyes, a continuous change in the monoclinic modification is observed: The intensity of reflexes (002) and (200) deepens, whereas the intensity of reflex (100) remains comparatively constant. Moreover, this process starts even in the lowest concentration interval (0.05–0.1%), and continues up to the highest concentrations of the acid dyes. A certain fluctuation is observed in the interval of the medium concentration (0.5–1.0 to 2.0%), which is probably due to the disorientation processes and the relaxation of the residual tension during the penetration of the acid dyes into the more solid (intra-fibrillar) amorphous regions of the structure. It is worth mentioning that in the samples dyed with Erionyl rubin 5-BLF (the WAXS diffractograms of PA6 samples dyed with Erionyl rubin 5-BLF are shown in Figure 3 as an example), the intensity of reflex (200) almost equals the intensity of reflex (002), which shows that a considerable improvement in the monoclinic structure in the crystal phase of the fibres occurs under the influence of this dye. In higher concentrations of the acid dyes, a certain decrease in the intensity of reflex (002) is observed, probably due to the general decrease in the solidity of the crystallites, caused by the increase in their defectiveness. Taking into consideration that in the high concentration interval the degree of crystallinity of polyamide multifilament yarn increases (Figure4), the decrease in the intensity of reflex (002) means that most probably the combination of the dye presence in the substrate and the 'cross-linking effect', connected with the formation of links of the type *PA-dye-PA*, provoke the formation of new crystallites on the one hand, but on the other hand hinder their growth into perfect crystal shapes.
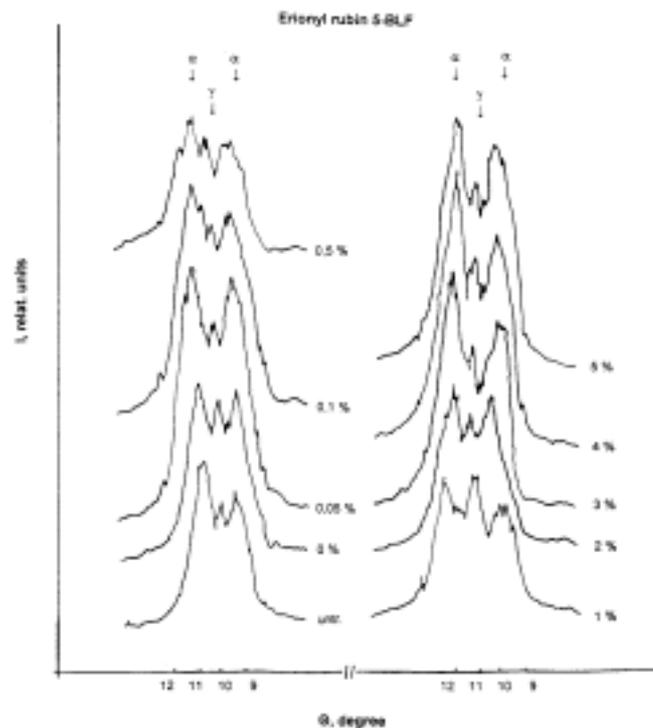

Figure 3. WAXS diffractograms of PA 6 samples dyed with Erionyl rubun 5-BLF

The intensive transformation of the crystal phase of the dyed samples throughout the entire interval of concentrations of acid dyes is also confirmed by **the modification of the inter-plane distances** (Figure 5) [22, 24].

The fact that the inter-plane distances in the hexagonal crystal lattices (d 100) remain virtually constant throughout the entire concentration area is interesting. More intensive changes in the inter-plane distances are registered in the crystal formations of the monoclinic modification (Figure 5, d 002 and d 200). This leads to the reasonable assumption that under the influence of acid dyes the existing monoclinic shape is perfected, and at the same time conditions are created for further crystallisation with a preference for the more stable α–modification. This assumption is confirmed by the increase in the intensity and the expansion of reflexes (002) and (200), a sign of the increase of the crystal areas with a monoclinic shape of the crystal lattice. On the other hand, the expansion of the crystal reflexes is interpreted by the increase in the defective areas in the crystallites and the presence of fine-crystal structure. This means that in the highest concentrations of acid dyes, conditions are created for rapid formation and growth of the new crystallites rather than for perfecting already existing crystal aggregates.

Table 1. Modification in the dimensions of the crystallites, determined for reflexes (002) and (100)

dye	C,%	dimensions of the crystallites, Å	
		/002/	/100/
Erionyl rubin 5-BLF	untr.	50.1	79.9
	0.00	49.3	71.0
	0.05	57.7	68.8
	0.10	63.6	63.9
	0.50	51.4	63.9
	1.00	60.4	62.4
	2.00	47.5	67.1
	3.00	51.5	61.9
	4.00	51.5	67.7
	5.00	50.5	75.3
Acidol orange 3 RL	0.05	61.2	79.9
	0.10	59.3	66.6
	0.50	47.7	66.6
	1.00	44.5	79.9
	2.00	47.2	72.6
	3.00	50.1	79.9
	4.00	53.5	76.1
	5.00	53.5	84.0
Acidol brillantgelb M-3GL	0.05	63.5	72.6
	0.10	63.2	88.7
	0.50	50.1	84.1
	1.00	47.2	84.1
	2.00	50.1	84.0
	3.00	46.6	84.1
	4.00	53.4	72.6
	5.00	47.2	79.9

The dimensions of the crystallites presented in Table 1, as determined from reflexes (002) and (100), are not real but imaginary. This is because when calculating them, neither the influence of the defects in the lattice nor the instrumental error in the shape of the reflexes have been taken into consideration. Besides, the values do not allow a correct interpretation to be made, because the modifications are within the framework of the method error.

From the data of **X-ray degree of crystallinity** presented in Figure 4, it is apparent that the treatment in the 'blind' bath results in a certain increase in the crystal phase, as compared with the untreated sample. This result is not surprising because it is known that the conditions of dyeing guarantee the transition of the polymer into a highly elastic state, in which the segmental mobility of the polymer chains is released, a prerequisite for the occurrence of relaxation processes which are different in nature and in the direction of their influence [1, 5, 6–8].

In the lowest concentrations of the acid dyes (0.05–0.1%), the degree of crystallinity increases considerably. This effect is probably due to the fact that under these conditions, which are far from the fibre saturation with dye, the dye molecules appear to be insufficient to compensate for the high potential energy of the active centres of the polyamide macromolecules, which favours the further arrangement of the polyamide structure. In the interval of the medium concentrations of acid dyes (0.5–1.0%), a decrease in the degree of crystallinity is observed again, which reflects the penetration of the dye molecules into the thicker intra-fibrillar amorphous areas, characterised by a higher thickness of the packing. Evidently the diffusion and fixation of the dye particles in the above-mentioned areas are connected with the breaking of a great number of inter-molecular links, whose energy cannot be compensated with the energy of the newly created links. In other words, conditions are created for increasing the segmental mobility and expanding the conformation set of PA-macro-chains, combined with a certain decrease of the existing structural tensions, increasing the 'looseness' of the structure and raising the disorientation of the intra-fibrillar non-crystal regions. With the increase of the dye presence in the fibres (2–5%), the degree of crystallinity steadily rises. Probably the so-called 'cross-linking effect' prevails here, involving the formation of additional inter-molecular links of the type *polyamide-dye-polyamide*, on the basis of ionic chemical bonds and physical forces (hydrogen bonds, and the van der Waals interactions which are various in character). This effect is accounted for not only by the pronounced affinity of acid dyes to the polyamide substrate, but also by the poly-functionality, typical for the dyes [9, 25–27], which predetermines the formation of bonds of different

character (chemical, physical) with the chain of the fibre-forming polymer. Moreover, the dye particle can interact with more than one polymer macro-chain; that is, the dye molecules appear to act like a peculiar material agent, which connects the adjacent polyamide macromolecules at the place of contact. This justifies the expectation that the 'cross-linking effect' should prove to be higher with the increase in the dye concentration. But this state also leads to a certain inhibition of the segmental mobility, which is eventually a prerequisite for the appearance of areas with a pronounced close order in the non-crystal sections of the structure, corresponding to more favourable conformations in respect to energy [2–8]. The arranged units which thus emerge can form nuclei of crystallisation, which is the probable cause of the additional crystallisation in the highest concentrations of acid dyes.
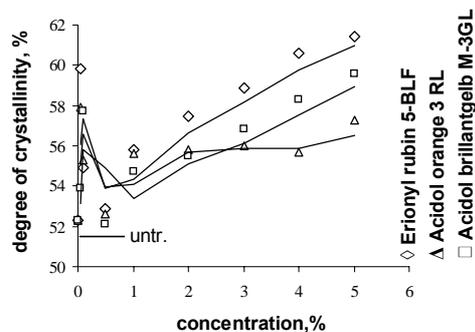

Figure 4. Modification in the X-ray - graph degree of crystallinity (α^{waxs}) depending on the concentration of the dyes used

From the **DSC investigations**, it is evident that acid dyes (and particularly their concentration) have a considerable influence upon the melting behaviour of the polyamide substrate (Table 2). All the curves of melting are characterised by one endothermic peak, which in general becomes sharper with the increase of the dye presence in the fibres, whereas its location moves towards the higher temperatures. An example of DSC-grams of PA6 samples dyed with Erionyl rubin 5BLF is shown in Figure 6. It is worth mentioning that in the 4–5% concentration of the dyes used, there is a tendency towards splitting the melting peak.

Table 2. DSK data for polyamide fibers depending on the different concentrations of acid dyes

dye	C %	T_m °C	ΔT_m °C	ΔH cal/g	α^{DSC} %
Erionyl rubin 5-BLF	untr.	219.4	17.2	20.7	37.8
	0.0	220.0	18.3	20.7	38.1
	0.05	228.9	15.4	24.8	45.4
	0.1	225.9	16.2	22.9	41.9
	0.5	219.5	21.1	20.0	37.6
	1.0	224.6	18.8	22.2	40.5
	2.0	227.5	16.0	24.2	44.3
	3.0	223.2	17.9	23.4	42.7
	4.0	228.2	19.3	24.0	43.9
	5.0	231.1	17.0	25.6	46.8
Acidol orange 3RL	0.05	226.4	16.5	23.4	42.9
	0.1	229.2	15.6	24.9	46.3
	0.5	221.5	20.1	21.0	39.2
	1.0	223.0	17.1	24.0	43.9
	2.0	228.9	18.3	24.6	45.0
	3.0	230.7	18.1	25.3	46.5
	4.0	229.0	17.3	27.0	47.8
	5.0	231.3	17.3	27.2	47.9
Acidol brillantgelb M-3GL	0.05	228.0	15.9	24.6	44.8
	0.1	229.2	16.7	24.7	45.2
	0.5	224.4	19.3	21.2	40.4
	1.0	222.1	17.1	23.8	43.3
	2.0	227.8	17.3	24.1	44.1
	3.0	227.7	18.1	24.7	45.3
	4.0	229.5	17.4	26.8	47.5
	5.0	229.2	17.8	27.7	48.5

It is known that the temperature of melting depends on the degree of crystallinity, as well as on the dimensions of the crystallites. But since according to the WAXS data the crystallites preserve comparatively close average linear dimensions (Table 1) while at the same time having different enthalpy of melting, it means that the change in the melting heat is due to the movement of the lower limit of the melting interval, which is determined by the respective degrees of crystallinity of the samples.

The data in Table 2 re-confirm that the concentration of acid dyes plays a major role in the direction and extent of the polymer structure's reorganisation during the dyeing process. The highest melting temperature and degree of crystallinity are observed in the lowest and highest concentration areas. Considering that the moving force of dyeing is the difference in the dye concentrations in the solution and the textile material, it is normal for the dye particles in the low dye concentrations to penetrate the most accessible amorphous areas of the structure. However, as the polyamide transition to a highly elastic state presupposes the system's aspiration towards a thermo-dynamic state, which is the most stable state for the concrete conditions, whereas the dye concentration is too low to essentially influence the high residual tensions in the structure, in the interval of the lowest dye concentrations the processes of structural transformation will obviously mainly involve enlarging the crystallites, provoked by their high free surface energy.
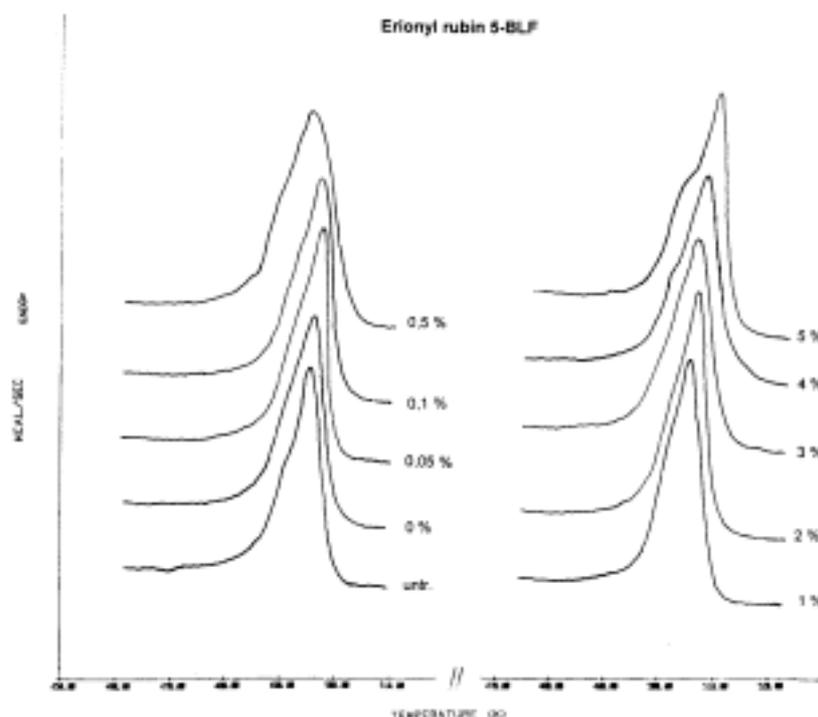
Figure 6. DSC – grams of PA 6 samples dyed with Erionyl rubun 5-BLF
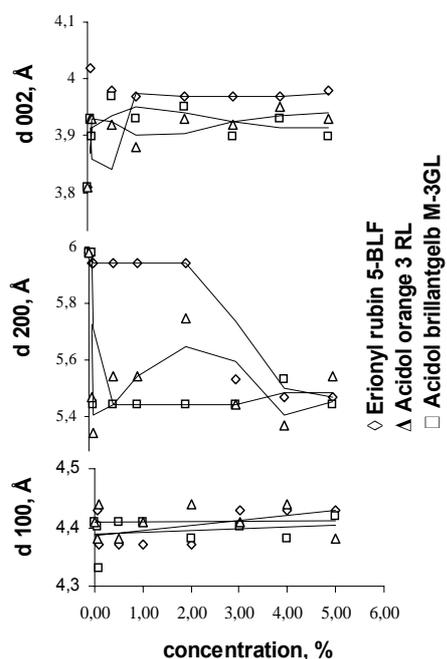

Figure 7. Modification in the inter-plane distances in the monoclinic and hexagonal crystal lattices depending on the concentration of the acid dyes

Moreover, the increase in the melting temperature reflects not only the increase in the sample's degree of crystallinity, but also the decrease of the defects in the crystal structure formed, and primarily an improvement in the monoclinic shape. This is confirmed by the considerable change in the inter-plane distances in the crystal formations with monoclinic modification of the lattice (Figure3). The view that the medium concentrations of acid dyes activate relaxation processes, connected with the decrease in the structure tensions and the increase in the disorientation of the thicker amorphous areas of the polyamide structure, is illustrated experimentally with the expansion of the interval of melting and the reduction of the enthalpy and temperature of melting. The appearance of a shoulder on the peak of melting, showing a tendency to split in the high concentration area, is most probably due to secondary crystallisation under the conditions of the high speed of nucleus-formation, resulting in a greater number of crystallites but which are smaller in size. It seems that the kinetics of crystallisation in the high concentrations of acid dyes is also influenced by the 'cross-linking effect' through which, on the one hand, the macromolecular segments are fixed in relatively compact and arranged areas; but on the other hand, the filling-up of a great part of the free volumes with dye particles is bound to limit the segment movement to a certain extent. This presupposes multi-centre surface nucleus-formation and the formation of small crystallites with rough surfaces, built up from chain folds [22, 24, 28, 29], which hinders the improvement of already-formed crystal formations.

It should be pointed out that the degree of crystallinity, determined from thermo-grams (α^{DSC}), is lower than the X-ray degree of crystallinity (α^{waxs}), but this is to be expected because during the heating of the samples in the calorimeter, the re-crystallisation processes overlap with the

endothermic effect of melting and lead to a decrease in the area of the melting peak . Nevertheless, it is worth paying attention to the fact that the character of modification in the degree of crystallinity, as determined by both methods, is preserved.
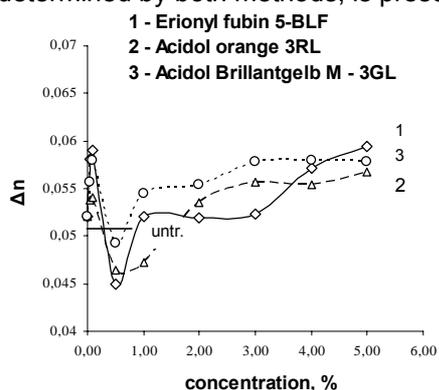

Figure 7. Modification in the birefringence depending on the concentration of the dyes used

From Figure 7, it is visible that dyeing with acid dyes considerably influences the **birefringence (Δn)** of polyamide multifilament yarn. It is noteworthy that the change in Δn is a function of the dye concentration. A similar correlation has also been ascertained by other authors, studying the influence of dyeing with acid, metal-complex and dispersed dyes upon the supra-molecular structure of polyamide fibres [10–12].

On the whole, the orientation of the dyed samples increases in comparison with the non-treated sample. This is to be expected, as Δn is a measure of the general orientation of the polymer, and it is entirely justified for its values to rise with the increase in the degree of crystallinity. Another factor which should have a positive effect on the birefringence is the *polymer-dye* interaction. This assumption is based not only on the data of the optical anisotropy of the dyes [30–32], which for steric reasons and because of the specifics of their interaction with the polyamide, become oriented in parallel to the polymer macromolecules, but also on the known fact of the additive character of the light anisotropy.

The growth of the general orientation of the dyed fibres throughout almost the whole concentration interval reflects the improvement of the crystal structure and the additional crystallisation (Figures 2 and 5), as well as the increasing influence of the 'cross-linking effect', which is increasingly evident with the increase of the dye presence in the substrate. An exception is made by the interval of the medium concentrations (about 0.5 to 2.0%), where a decrease in Δn is recorded, although the degree of crystallinity of the dyed samples remains higher than that of the non-treated ones. It is most likely that the orientation of the samples in the area of the medium concentrations is basically affected by the relaxation processes which occur during the penetration of the dye particles into the inter-lamellar amorphous regions of the polyamide. Apparently the dye concentration is still insufficient to enable the 'cross-linking effect' they cause to compensate for the disorientation increase and the decrease of the energy of the inter-molecular interaction, fixing the polyamide chains of the non-crystal areas in the preferred oriented state.

It is natural to expect the specifics of the chemical composition of the dyes to contribute to the fluctuation in the values of the birefringence, but this influence can be considered insignificant, bearing in mind the similar character of the modification of Δn as a function of the concentration of the dyes used.

The influence of acid dyes upon some physico-mechanical properties of polyamide fibres (multifilament yarn and fabric)

The physico-mechanical properties of polyamide fibres are predetermined to a great extent by the initially formed supra-molecular structure, but the final complex of properties is formed during the process of additional thermal treatments, where dyeing plays a significant part [1.2.18.19.31.32].

As shown in the previous analyses, the various structural indices of the fibres change to a greater or lesser degree in the process of dyeing, namely the dimensions and orientation of the crystal formations, the thickness of the macromolecule packing in the crystal and amorphous areas, the molecule orientation, the inner tensions depending on the elasticity of the polymer chains, and last but not least, the energy of the inter-molecular interaction.

It has even been established that acid dyes (and particularly their concentrations) are a complex factor in respect to the polyamide structure, and the effectsof the dye presence in the substrate frequently have conflicting influences. Therefore it is natural to expect that the specifics of the modification in the supra-molecular structure will have a typical influence upon the physico-mechanical properties of the samples.

This is well illustrated in Figures 8 and 9, which show the dependency of the **tenacity and elongation at break** on the concentration of the dyes used.

The data show that the very treatment of the samples in a 'blind' bath, irrespective of the presence or absence of dye, has a definite reflex upon the mechanical indices. The tenacity of the

samples decreases from 30.9 cN/tex to 30 cN/tex, whereas the elongation at break increases from 19.1% for a non-treated sample to 22% for the samples treated in a 'blind' bath. These changes increase in the lowest concentrations of acid dyes.
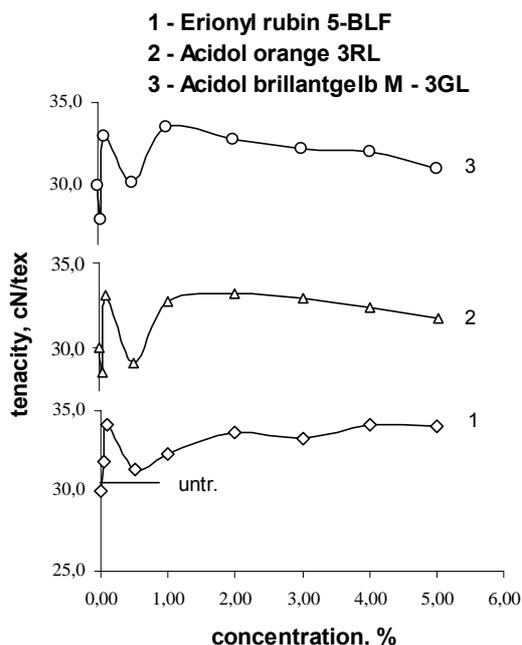
1 - Erionyl rubin 5-BLF
2 - Acidol orange 3RL
3 - Acidol brillantgelb M - 3GL

Figure 8. Modification in the tenacity depending on the concentration of the dyes used

It is known that when a crystallising polymer is subjected to heating at temperatures higher than that of its glass transition, the occurrence of two concurrent processes is possible – crystallisation and relaxation (disorientation). The predominance of one or the other depends in this case on the general state of the system and the dye concentration, as affirmed above. It seems that the enlargement of the crystal aggregates under the influence of minimal quantities of dye molecules leads to an increase in the number of chains connected with one or both ends to the adjacent crystallites, or to the same plane of a certain crystallite. This causes a local concentration of tensions along the length of the separate chains, and increases the differences in the lengths of the polymer macromolecules in the amorphous areas; in other words, the number of the pre-strained and greatly stretched chains increases, and these break quickly when loaded. Furthermore, the improvement in the crystal lattice of the monoclinic modification is connected with pushing the defective parts towards the ends of the crystal formations; this in turn increases the disorientation in the amorphous areas of the structure, and leads to an increase in the number of the polyamide macromolecules with folded conformation. This causes an irregular distribution of the deformation tensions in the fibres, as well as an increase in the number of sensitive places susceptible to outside factors of influence. The natural result of these changes is a decrease in the tenacity. On the other hand, the increase in the perfection of the crystallites and th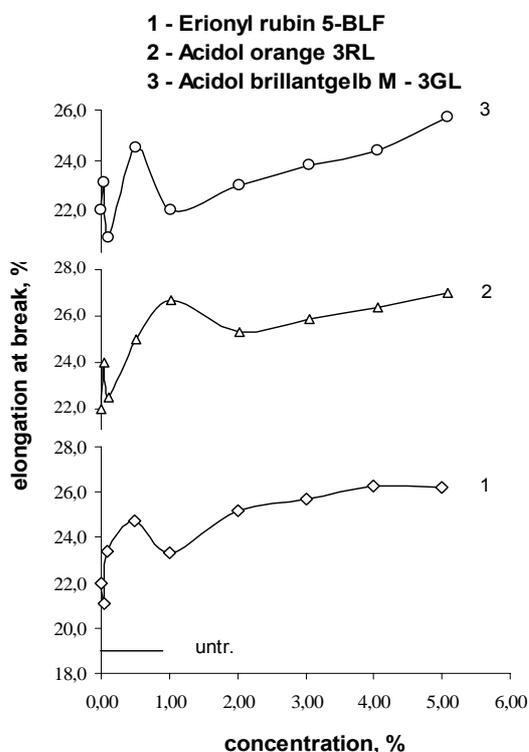e amassment of crystal defects in the amorphous inter-lamellar layers [6-8, 21-24, 28] is accompanied by a relaxation* in the amorphous regions, connected with the expansion of the conformation set and the increased freedom of movement of the polyamide chains. This is a pre-condition for the elongation at break of the samples. The sample, dyed with 0.05% Erionyl rubin 5-BLF, is an exception for which both increase in tenacity and elongation at break are recorded simultaneously. Probably in this case, the chemical structure of the dye molecule has a specific influence upon the equilibrium improvement – disorientation, which results in an optimal correlation between the rates of the two processes. The intensive relaxation in the amorphous sections of the substrate, together with the concurrent improvement of the stable α–modification, allows the increase in the number of the moderately folded macromolecules, which assume the loading simultaneously when outside mechanical exertion is applied. Along with this, the moderately folded molecules allow considerable deformation of the fibres without being broken, i.e. the deformation is elastic in its greater part. This effect is strengthened with the 0.1% concentration of the dye, and similar behaviours are observed with the other two dyes.

1 - Erionyl rubin 5-BLF
2 - Acidol orange 3RL
3 - Acidol brillantgelb M - 3GL

Figure 9. Modification in the elongation at break depending on the concentration of the dyes used

Another more substantial change in the main physico–mechanical properties is observed within the concentration interval 0.5–1.0%, where the relaxation processes predominate, albeit in the thicker amorphous areas of the structure. This is to be expected, because in the higher dye concentration of the bath, the diffusion of the dye molecules into the less accessible sections of the polyamide structure becomes possible. The very penetration of the dye particles into the above-mentioned areas is connected with the destruction of a great part of the stable inter-molecular bonds, i.e. with decreasing the energy of the inter-molecular interaction, increasing the segmental mobility and on the whole favouring the disorientation. The relaxation effect in the intra-fibrillar amorphous areas involves expanding the conformation set and decreasing the interior tensions, and leads to increasing the number of the chains which are capable of undergoing elastic deformation. This results in an increase of the elongation at break, and a reduction of the tenacity of the samples (Figures 8, 9).

The modification of the tenacity and elongation at break in the area of high concentrations of acid dyes (2–5%) is less pronounced, probably due to the mutual compensation of the effects described. Nevertheless, the tendency to decrease the values of tenacity, while respectively increasing the elongation at break, is preserved to a certain extent. This behaviour of the dyed samples is somewhat pre-determined, not only by the additional crystallisation, but also by the influence of the 'cross-linking effect'. As mentioned earlier, the 'cross-linking effect' on the one hand promotes the activation of the crystallisation processes, but on the other hand accounts for the formation of small-crystal structures characterised by many defective areas. The great number of defects in the crystal stage, in combination with the concurrent relaxation phenomena in the amorphous regions of the structure, is reflected in the recorded decrease of the strength characteristics of the fibres.

It is worth pointing out that, despite the recorded fluctuation in the course of the measured indices, the mechanical properties of the dyed samples as a whole are higher than those of the non-treated polyamide multifilament yarn.

The results obtained for the **angle of restoration after creasing (ARAC)** completely match the profile of the structural modification which occurs during dyeing.

The modification of ARAC has a characteristic maximum in the lowest dye concentrations, with a consequent decrease in the medium concentration area, and a light increase or maintenance of the values in the high concentrations of acid dyes (Figure 10).
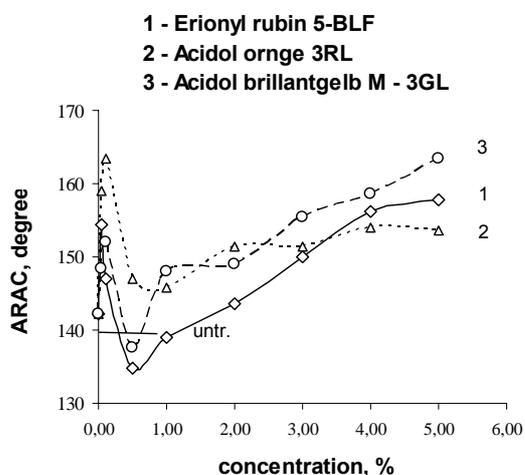
1 - **Erionyl rubin 5-BLF**
2 - **Acidol ornge 3RL**
3 - **Acidol brillantgelb M - 3GL**

Figure 10. Modification in the ARAC of the dyed samples as a function of the dye concentration

It should be emphasised here that the factors determining the growth of the ARAC are of a quite different nature. On the one hand, the high values of ARAC are due to the high elasticity of the textile material; on the other hand, in the presence of pre-conditions for plastic deformation of the samples, the ARAC increases through the creation of stable inter-molecular links, which ensure the return of the polymer chains to their initial position after the removal of the deformation load.

The increase in the crease resistance of the samples under the influence of the minimal concentrations of the dyes used reflects the high degree of relaxation, reached in the inter-fibrillar amorphous areas of the substrate. Before undergoing the repeated washing at high temperatures which is characteristic for the period of its exploitation, polyamide fibres are characterised by considerable residual tensions. These tensions are distributed highly irregularly both among the different layers and among the separate molecules within one layer. There are completely strained molecules, moderately folded and moderately strained molecules, as well as molecules folded to their equilibrium state, i.e. not strained at all. During the dyeing process, an intensive relaxation of the supra-molecular structure occurs, and a clear and precise tendency is observed, irrespective of the proceeding modifications. The most strongly strained molecules are folded partially by different mechanisms, and are transformed into moderately folded ones. The uniformly folded molecules, in turn, most probably participate in the processes of consolidation towards the adjacent supra-molecular formations, as well as in the process of re-crystallisation; the remaining free areas are transformed into moderately folded ones. Thus the predominant state of the molecules in the amorphous areas becomes moderately folded, i.e. the differences of the lengths of the separate molecules decrease,

and their transition to more favourable conformation states from an energy point of view leads to a reduction in the interior tensions. This allows considerable deformation (of a predominantly elastic nature) of the fibres . In other words, in the area of low concentrations of acid dyes the first of the factors is manifested which contribute to the increase in the crease resistance-increased elasticity of the samples.

The influence of the other factor, namely the creation of stable inter-molecular links, which also leads to an increase in crease-resistance, is well observed in the highest concentration interval (4–5%), as the 'cross-linking effect' starts to show itself markedly in the highest dye concentrations.

In the medium concentrations of acid dyes (0.5 to about 3%), fluctuations are observed in the course of the curves, as well as a decrease in the ARAC values; these are the result of limiting the number and length of the folded sections in the amorphous areas??[[respectively of the possibility of]] elastic deformation occurring. Furthermore, during the diffusion of the dye particles in the thicker intra-fibrillar amorphous areas, some of the stable inter-molecular links are destroyed, and the molecules of acid dyes fill up a considerable part of the free volumes in the inter-lamellar spaces. Thus the segmental mobility is limited, and a definite plasticisation of the system is reached because the newly-formed inter-molecular links of the type *polymer-dye-polymer* are still insufficient to return the polyamide chains to their initial state after the deformation loading is removed.
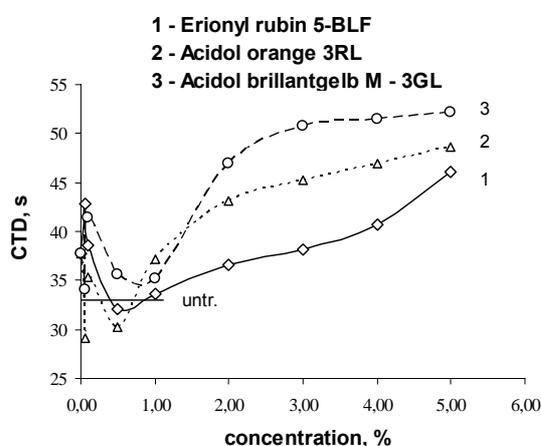

Figure 11. Modification in the critical time of dissolution depending on the concentration of the dyes used

On the basis of this data, it can be concluded that the correlation between the influences with opposite signs is a function of the concentration of acid dyes in the polyamide substrate, and this can vary within a wide range. This correlation depends on the size of the dye molecules, and accounts for some differences in the values obtained with the different dyes. Still, the fact that the character of the dependency is preserved for all samples under investigation is indicative remarkable.

The assumptions made about the mechanism of influence of acid dyes upon the supra-molecular structure and the physico-mechanical indices of polyamide fibres are also confirmed by the change in the **critical time of dissolution (CTD)**.

This analysis well characterises the summary effect of the decrease in the solidity and the destruction of the inter-molecular links, as well as the congestion and creation of stronger inter-molecular contacts in the amorphous areas of the structure with different thicknesses.

Figure 9 shows the influence of the dye presence in the fibres upon CTD. The decrease in the dissolution time in the lowest concentrations of acid dyes (0–0.1%) reflects the increase in the 'looseness' and the decrease in the number and strength of the inter-molecular links in the inter-fibrillar amorphous areas of polyamide. The relaxation effect involves decreasing the time for the penetration of the solvent into the fibrous structure, and increasing its receptivity towards various low-molecular compounds.

In the entire next interval up to maximum concentration, the CTD rises, which indicates that the 'cross-linking effect' gradually prevails, and also that the structure has solidified due to the re-crystallisation processes having occurred. The minimum in the run of the curve, which is visible in the ~0.5%-concentration, is the result of the second phase of the dye penetration into the thicker amorphous areas, accompanied by a loosening of the structure.

Note: Here, and in most cases, 'relaxation' means the disorientation of the macromolecules. In fact, this process is a partial case, as the relaxation processes refer to the transition from one equilibrium state into another.

Conclusion

The results of the analyses prove that the concentration of acid dyes is a major influence on the direction and degree of the structural transformation of polyamide substrate, with a natural reflex upon the physico-mechanical properties of the fibre-forming polymer. It is worth pointing out that the obtained dependencies have a similar character, which hardly depends on the type of the dyes used,

in spite of the differences in their chemical structure, and the shape & size of their molecules. This suggests that to a great extent the role of the dye molecules comes down to the role of the poly-functional particles with their own volume. Moreover, they are not necessarily poly-functional just because they have more than one functional group interacting with the polymer in a specific way. In brief, our understanding of the behaviour of the polymer and the dye during the process of dyeing, as far as it differs from the quoted literature, is as follows:

1. Irrespective of the rather complex character of the supra-molecular structure of the polyamide, two kinds of areas with relatively low arrangement are observed therein – those between the supra-molecular formations (inter-fibrillar), and those in the supra-molecular formations (intra-fibrillar or inter-lamellar). Naturally the first have much lower solidity. Both the dyeing and mechanical properties depend primarily on the state of these areas, as has been proved by the experiment.

2. The penetration of the dye molecules into the fibre mass is accompanied by two phenomena, which have opposite effects upon the structural characteristics and the mechanical properties. The first is the diffusion of the dye molecules among the polymer molecules, accompanied by a loosening and relaxation respectively of the polyamide structure. The second is the formation of bonds of the type *polymer-dye*. In our opinion, the idea that these bonds in acid dyes are only of an ionic character known to us is not fully accurate. On the contrary, besides them, hydrogen bonds and links on the basis of the van der Waals interactions of a universal character are formed. Their strength is naturally much smaller than that of the ionic bonds, but because of their considerable number, their ??[[total energy]] is considerable. In all cases, this means that links of the type *polymer-dye-polymer* emerge, irrespective of the number of the functional groups (forming ionic or other links) typical for a certain dye. This in turn shows that each dye molecule plays the role of a cross-linking agent in the polyamide structure, besides that of a colouring agent. As a rule, the fixation of the polymer molecules with such a net of physical contacts influences the mechanical properties in a way opposite to the relaxation of the structure.

In order for the relaxation effect to be noticed, a comparatively low dye concentration is necessary, because a small number of dye molecules are enough to affect the most strained links in the structure. On the contrary, in order for the 'cross-linking effect' to be noticed, a comparatively higher dye concentration is necessary because the hydrogen and the van der Waals links are weaker; furthermore, they have to compensate for the destruction of part of the inter-molecular links during the relaxation. Because of that, the two effects manifest themselves in different dye concentrations in the fibre, and lead to the recorded specific modification in the supra-molecular structure of the samples.

The characteristic features of the structural modifications in the wide interval of concentrations of acid dyes naturally influence the studied physico-mechanical properties of polyamide fibres as well.

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