Evaluation of the Sorption Phenomena Mechanism of Polyacrylonitrile Fibres for Selected Dyes in the Aspect of Structural Changes Resulting from Thermal Stabilisation Processes

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DOI: 10.5604/01.3001.0013.5863

Abstract
The aim of the research was to analyse the influence of the initial heat treatment of polyacrylonitrile fibres on their sorption properties in relation to selected basic and disperse dyes, in order to select the dyeing variants most beneficial from the point of view of increasing the sorption capacity of commonly used dyes and improving the dyeing process. Research was carried out on a fibre produced on an industrial scale, using dyes of basic application importance, which differ in the diffusion properties of the molecules and the mechanism of binding with the fibre material. Thermal treatment of the fibre was carried out in various media (air, water, steam), with various variants of the temperature and its duration, i.e. under the conditions commonly used in fibre preprocessing processes and their “improvement”. During the research, several different measurement methods were used to assess changes in the molecular and supramolecular structure of the fibre material: the infrared absorption spectroscopy method, the critical fibre dissolusion measurement method, the densitometric method, and the interferential polarisation microscopy method. Fibre sorption changes resulting from the modification of the structure of the fibre under the influence of thermal treatment were analysed from the point of view of improving the efficiency of dye use and shortening the dyeing time based on commonly accepted values of the sorption index C₀ and kinetic sorption index: t₀₁ for basic dyes and t₀₂ for disperse dyes.

Key words: polyacrylonitrile fibre, molecular and supramolecular structure, FTIR, CDT methods, heat treatment, sorption, basic dyes, disperse dyes.

Introduction
The high temperature processing of polyacrylonitrile, leading to the rebuilding of their matter as a result of crosslinking, cyclisation, dehydrogenation and other reactions, has been the object of interest of many authors [1-14]. Most studies are related to obtaining carbon and high-performance fibres. In the studies available, data are missing on the influence of thermal treatment carried out at lower temperatures and in different media on the changes occurring in the fibre structure and their properties in the aspect of the widespread use of fibres as a substitute for wool fibre, i.e. physico-chemical properties such as dyeability and springiness.

The thermal treatment to which fibres are subjected in the processes of manufacturing and finishing can lead to changes in the molecular and supramolecular structure of their matter. The molecular structure may be followed by the reconstruction of macromolecules, including a change in the conformation of their chains and side groups, leading to changes in the molecular coherence of the fibre matter. In the chemical supramolecular structure, there are changes in the crystalline phase content, overall orientation, crystallographic systems and orientation of crystalline aggregates [10-17]. The range of changes and their direction varies depending on the type of heating medium used, as well as on the temperature, heating time and the dynamic state of the heated fibre [18, 19].

Properly carried out thermal stabilisation allows to achieve changes in the structure of the fibre material and to obtain new, economically advantageous physical and physico-chemical properties of fibres, including better liquid sorption and affinity to dyes. In industrial processes, it allows for shortening the dyeing time, as well as reducing dye consumption and the amount of wastewater discharged, thus achieving significant economic savings and improving the ecology.

In the case of polyacrylonitrile fibres, which are a widespread substitute for wool fibres due to their high level of heat protection, their physico-chemical properties are mainly affected by the amount and diversity of chemical groups present in the fibre-forming material, derived from comonomers of acrylonitrile, their chemical nature and spatial shape. They are not only active centres that have the ability to interact with dye molecules (sorption ability), but they also affect the presence of microcapillaries, free spaces and non-crystalline areas of the fibre, which co-determine the diffusion of dyes [20-24].

Experimental
Materials
Commercial polyacrylonitrile fibre known as Crumeron was used for the study. Characteristics of the fibre, including chemical composition and manufacturing technology, are listed in Table 1.

| Fibre trade name | Crumeron (Hungary) |
|------------------|--------------------|
| Producer | Zoltek |
| Chemical composition of the fibre material | Acrylonitrile 91%, Methyl acrylate 8%, Sodium allylsulfonate 1% |
| Polymerisation method | Solution method |
| Solvent | DMF |
| Spinning method | Wet process |

Table 1. Characteristics of the chemical composition and production technology of Crumeron polyacrylonitrile fibre.
Palanil Gelb 3G (disperse dye), with a high dipole moment and linear structure, expanded molecule (number according to C.I. 11/62015), with the formula (number according to C.I. 48054), with the formula C.I. Basic Yellow 28 (basic dye), with a structure typical of this group of dyes.

Thermal treatment in air, water and steam was carried out using fibres in an unstrained state and the following apparatus:
- a chamber for thermal tests: KBC – 125G from WAMED – for treatment with hot air,
- pressure dyeing apparatus: AHIBA POLYMAT – for treatment with water at 100 °C and 120 °C,
- a steam steriliser: STS – for treatment with steam.

The thermal treatment program is presented in Table 2.

| Temperature, °C | Time, min | Temperature, °C | Time, min | Temperature, °C | Time, min | Pressure, MPa |
|----------------|-----------|----------------|-----------|----------------|-----------|--------------|
| 180            | 5         | 100            | 15        | 120            | 15        | 0.1          |
| 220            | 2         | 120            | 15        | 134            | 15        | 0.25         |

As can be seen from the data presented in Table 1, Crumeron fibre is made from a three-component copolymer.

The presence of a large number of polar -CN groups in acrylonitrile macromolecules affects the high molecular coherence of the fibre material. In order to “loosen” the fibre structure and improve dye diffusion conditions, comonomers were built into the macromolecules of the acrylonitrile: methyl acrylate and sodium allylsulfonate.

Methyl acrylate is characterised by relatively low polarity and undergoes a hydrolysis reaction, which can be catalysed by both acids and alkali [25].

As a result of the hydrolysis mentioned, carboxylic groups may appear in macromolecules of the fibre material. The presence of -COOH and -SO₃Na groups, which undergo dissociation in an aqueous environment, allows the formation of ionic bonds with cationic dyes. The “loose fibre structure” and the polar nature of the material make it possible to use non-ionic dyes for dyeing the fibre, so-called disperse dyes.

Changes in the sorptive capacity of the test fibre subjected to thermal treatment in variants of the stabilising treatment used in industrial conditions, were examined based on the following dyes:
- C.I. Basic Yellow 28 (basic dye), with a structure typical of this group of dyes (number according to C.I. 48054), with the formula (Figure 1).
- Celliton Rosa FF3B (disperse dye), with a small dipole moment and spatially expanded molecule (number according to C.I. 11/62015), with the formula (Figure 2).
- Palanil Gelb 3G (disperse dye), with a high dipole moment and linear structure (number according to C.I. 11/62015), with the formula (Figure 3).

The dye diffusion conditions, comonomers build into the macromolecules of the fibre material, trimer allylsulfonate.

Changes in the molecular structure were assessed by means of:
- IR absorption spectroscopy,
- a measurement method for the critical fibre dissolution time in selected solvents to assess changes in the molecular cohesion energy of the fibre material.

Changes in the fibre’s physical microstructure were analysed using: 

![Figure 1. C.I. Basic Yellow 28.](image)

![Figure 2. Celliton Rosa FF3B.](image)

![Figure 3. Celliton Rosa FF3B.](image)
the densitometric and IR absorption spectrometric methods for the assessment of changes in the para-crystalline phase,

interferential-polarisation microscopy for the determination of fibre optical birefringence as a basis for the assessment of changes in the fibre’s general orientation.

Fourier transform IR (FTIR) spectroscopic measurements of the fibre’s molecular and supramolecular structures

FTIR spectroscopic analysis was carried out using the transilluminating technique on tablet specimens containing 1% of powdered fibre, with the use of a FTIR spectrophotometer – Nicolet 6700 coupled with the “The Thermo Scientific” company’s control unit. FTIR absorption spectra were recorded within a wavelength range of 4000 cm⁻¹ and 600 cm⁻¹ in the following systems: T = f(1/λ), A = f(1/λ) [28-30].

The spectra obtained constituted the basis for the determination of absorbance A of selected bands, whose values were used to interpret changes in the fibre molecular structure.

Based on the IR absorption spectra of fibres, values of the para-crystallinity factor were also determined [31] relating the band of the molecular order with a wave number of ~775 cm⁻¹ and ~1073 cm⁻¹. The para-crystallinity factor was calculated by means of the following Equation (1):

\[ x_p = \frac{A_{775}}{A_{1073}} \]

Where, \( A_{775} \), \( A_{1073} \) – absorbance of bands at ~775 cm⁻¹ and ~1073 cm⁻¹, respectively [32].

Examination of the fibre’s molecular cohesion based on the assessment of the CDT of the fibre

Changes in the fibre molecular cohesion were assessed by means of microscopic observation of fibre dissolution in N,N – dimethylformamide (DMF). Measurements were carried out at a constant temperature (50 °C) owing to the use of a microscope with a heated table (Böethius). The disappearance of the fibre image was accepted as the end of the fibre dissolution [33].

| Table 3. Results of measurements of the absorbance, critical dissolution time, density and optical birefringence of the fibres before and after heat treatment. |
| --- |
| **Parameters of heat treatment** |
| **Medium of thermal treatment** |
| **Air** | **Air+ water steam** | **Water** |
| **Temperature and time of thermal treatment** | **Temperature and time of thermal treatment** | **Temperature and time of thermal treatment** |
| 180 °C, 5 min | 220 °C, 2 min | 120 °C, 15 min |
| Designation of heat treatment variant | C1 | C2 | C3 | C4 | C5 | C6 | C7 |
| Measurement results | | | | | | | |
| Absorbance of band at ~775 cm⁻¹ | 0.044 | 0.058 | 0.045 | 0.042 | 0.049 | 0.045 | 0.041 |
| Absorbance of band at ~1073 cm⁻¹ | 0.127 | 0.176 | 0.127 | 0.130 | 0.136 | 0.133 | 0.126 |
| Critical time of dissolution [s] | 14.8 | 24.7 | 31.4 | 58.17 | 106.8 | 28.2 | 32.8 |
| Fibre’s real density [g/cm³] | 1.1791 | 1.1820 | 1.1839 | 1.1804 | 1.1804 | 1.1784 | 1.1782 |
| Optical birefringence | -0.0016 | -0.0023 | -0.0024 | -0.0021 | -0.0033 | -0.0025 | -0.0041 |

| Table 4. Values of paracrystallinity, corrected absorbance and optical birefringence indexes of fibres before and after thermal treatment. |
| --- |
| **Parameters of heat treatment** |
| **Medium of thermal treatment** |
| **Air** | **Air+ water steam** | **Water** |
| **Temperature and time of thermal treatment** | **Temperature and time of thermal treatment** | **Temperature and time of thermal treatment** |
| 180 °C, 5 min | 220 °C, 2 min | 120 °C, 15 min |
| Designation of heat treatment variant | C1 | C2 | C3 | C4 | C5 | C6 | C7 |
| Values of factors concerning the molecular and physical microstructure | | | | | | | |
| Corrected absorbance of band at ~2240 cm⁻¹ | 0.2684 | 0.3068 | 0.2518 | 0.2717 | 0.2356 | 0.2545 | 0.2472 |
| Para-crystallinity index \( x_p \) | 0.49 | 0.51 | 0.49 | 0.50 | 0.50 | 0.48 | 0.48 |
| Optical birefringence, corrected density | -0.0014 | -0.0019 | -0.0020 | -0.0018 | -0.0028 | -0.0021 | -0.0035 |

| Table 5. Values of sorption index \( C_s \) and kinetic sorption indexes: \( t_{0.5} \) for basic dye and \( t_{0.7} \) for disperse dyes. |
| --- |
| **Variant of heat treatment** | **Dye C.I. Basic Yellow 28** | **Dye Celliton Rosa FF3B** | **Dye Palanil Gelb 3G** |
| **Cₚ** mg/g fibre | **tₚₜ** s | **Cₚ** mg/g fibre | **tₚₜ** s | **Cₚ** mg/g fibre | **tₚₜ** s |
| C1 | 21.4286 | 22.0 | 6.6529 | 25.0 | 0.8286 | 15.0 |
| Air, 180 °C, 5 min |
| C2 | 21.0936 | 19.5 | 6.1368 | 20.0 | 0.9148 | 11.0 |
| Air, 220 °C, 2 min |
| C3 | 26.6619 | 12.5 | 7.6304 | 8.0 | 1.0140 | 8.5 |
| Air + water steam, 120 °C, 15 min |
| C4 | 28.6995 | 16.5 | 7.0471 | 14.0 | 1.0506 | 10.0 |
| Air + water steam, 134 °C, 15 min |
| C5 | 29.8440 | 14.0 | 7.5750 | 8.0 | 1.0093 | 8.0 |
| Water, 100 °C, 15 min |
| C6 | 15.2218 | 34.5 | 6.0930 | 58.0 | 0.9585 | 27.0 |
| Water, 120 °C, 15 min |
| C7 | 6.7832 | 16.0 | 5.9717 | 21.0 | 8.8827 | 9.0 |
Figure 4. Dyeing curves and changes in values of the sorption index and kinetic dyeing index t₀.₅ of Crumeron fibre subjected to a thermal medium and dyed with C.I. Basic Yellow 28.

Measurement of the content of PAN fibre ordered (para-crystalline) material by the densitometric method

Measurement of the content of PAN fibre ordered (para-crystalline) material was made on the basis of the para-crystallinity theory of Lindenmeyer and Hosemann [34]. The relationship between the real density and fibre mass crystallinity degree was determined on the basis of the following Equation (2):

\[ x = \frac{d_c (d - d_a)}{d (d - d_{akr})} \]  

(2)

where:
- \( d \) – fibre’s real density, g/cm³,
- \( d_{akr} \) – ordered (paracrystalline) material density, g/cm³,
- \( d_a \) – amorphous material density, g/cm³.

For determination of the fibre’s para-crystallinity degree according to the equation above, the following values were used: \( d_{akr} = 1.262 \text{ g/cm}^3 \) and \( d_a = 1.110 \text{ g/cm}^3 \) [35].

Measurement of the fibre’s real density was made by the flotation method with the use of a gradient column maintained at a temperature of 25 °C.

Measurement of the fibre’s overall orientation by the optical method (split image technique)

The fibre’s optical birefringence parameters were determined by measuring the directional light refraction coefficients for the fibre \( (n_\parallel, n_\perp) \) and then calculating the difference in their values \( (\Delta n) \). The technique of a homogeneous interferential field with a completely split image was used, utilising an MPI-5 interferential-polarisation microscope from PZO [36, 37].

Average values of the optical birefringence were used to calculate the optical birefringence, corrected in terms of density, according to the formula Equation (3):

\[ \Delta n = \frac{\Delta n_{cor}}{n} \]  

(3)

which was used as an index that characterises the overall fibre orientation [35], and \( \Delta n \) – the fibre’s optical birefringence, and \( d \) – the fibre density, determined by the densitometric method.

Fibre dyeing methodology

Dyeing of the fibre was carried out on AHIBA POLYMAT apparatus. Stable conditions of dye sorption during the entire dyeing cycle were provided using a 100:1 multiplicity bath containing 10% dye relative to the weight of the dyed fibre. Dyeing schemes used in industrial practice were utilised.
It is possible to observe a reduction in the intensity of the 2240 cm\(^{-1}\) band, which is correlated with the -CN group, for fibres treated with water at both temperature variants and in air and steam, at 220 °C and 134 °C, respectively. This indicates a stronger involvement of these groups in intermolecular interactions, and in the case of thermal treatment with hot air also in the cyclisation of nitrile groups, which affects the increase in molecular cohesion of the fibre matter and limits the availability of active centers for molecules of dye, moving in the fibre.

An increase in the molecular coherence of the fibre matter is confirmed by the changes in the value of the critical time of dissolution. An increase in the value of this index is observed for all time and temperature variants of the heat treatment.

Dyeing with a basic dye was started at temperature 30 °C. The bath was heated gradually at 3.5 °C per minute. After obtaining a temperature of 95 ± 0.5 °C, the test fibre was dyed for 20, 60 and 90 minutes. Dyeing of the fibre with a disperse dye was carried out at the same temperature, using time variants of 10, 20, 60, 120 and 240 minutes. The dyed fibre samples were rinsed in distilled water and then dried under room conditions. The concentration of the dye in the fibre was determined by performing colorimetric measurements using a SPEKOL11 spectrophotometer from the ZEISS company.

Results and discussion

Results

The results of measurements and values of the determined indexes used to assess changes in the fibre structure parameters caused by thermal factors are presented in Tables 3 and 4.

Table 5 presents values of the C\(_b\) sorption and kinetic sorption indexes, which were used to assess the dyestuffs’ sorption ability.

Results of fibre dyeing tests

Dyeing curves and changes in the values of sorption indexes are shown in Figures 4 to 6, allowing to conclude on the effect of the initial heat treatment on the sorption properties of the fibre tested in relation to selected dyes.

Changes in the molecular and supramolecular structure of the fibre tested

The initial thermal treatment of the fibre tested caused changes in the molecular and supramolecular structure of its fibre matter.

Figure 5. Dyeing curves and changes in values of the sorption index and kinetic dyeing index \(t_{0.7}\) of Crumeron fibre subjected to a thermal medium and dyed with Celliton Rosa FF3B.
ment. A particularly high increase in CDT values is observed for steam treated fibres.

The rebuilding of the physical fibre microstructure was analysed in the aspect of changes in the paracrystallinity and overall orientation of matter. The values of paracrystallinity indexes $X_m$ and $X_{IR}$ obtained show small changes in the content of paracry stalline matter, and hence their low impact on the sorptive properties of the fibre. This is the effect of heating the fibre in an unstrained state [35] at a relatively low temperature of the media. This method of treatment also resulted in significant changes in the optical birefringence. Thermal treatment for all variants leads to a decrease in the value of this index, which means a deterioration in the overall orientation of the fibre tested, being a consequence of the process of disorientation of the macromolecules that occurs in the amorphous and mesomorphic phases.

Changes in dyeability of the tested fibre

It was found that the value of the sorption index $C_b$ obtained for the initial fibres tested dyed with a basic dye, is significantly higher than the values of index $C_b$ obtained for fibres dyed with disperse dyes. Differences in the values of the indexes analysed result from the different mechanisms of binding of the dyes investigated with polyacrylonitrile fibres. Better cationic dyeing results were obtained due to the possibility of formation, in addition to van der Waals bonds, which are the basic bonds in the dyeing of synthetic fibres with disperse dyes, ionic bonds between dye cations and active centres of the fibre-forming polymer [20]. Differences were also observed in the sorption indexes of fibres dyed with suspension dyes, which result from the different structural features of these dyes. From the point of view of colour saturation, it is more effective to dye Crumeron fibre with a non-linear molecular structure and lower dipole moment (Celliton Rosa FF3B), which increases its diffusion and ‘makes binding to the fibre matter easier’.

The dyeing curves shown in Figures 4, 5 & 6 indicate that the thermal treatment of Crumeron fibre applied before dyeing has an impact on the change in kinetics of dyeing processes and on the sorption capacity of the fibre in relation to all dyes tested.

The direction of changes observed depends on the parameters of the thermal treatment. The decrease in the number of free CN groups, tantamount to an increase in molecular cohesion, while deteriorating the overall orientation of the fibre material resulted in:
an increase in the sorption index and dyeing kinetics in the case of Palanil Gelb 3G dye,

an increase in values of the Cb index and a reduction in sorption kinetic index values in the case of disperse dye Celliton Rosa FF3B and C.I. Basic Yellow 28 for fibres thermally treated in steam and air at 220°C. For other variants of thermal treatment, the sorptive capacity of the fibre decreased,

a large increase in the kinetic sorption index of all dyes tested for fibre treated in water at 100°C.

The direction of changes in fibre dyeabil-
ity indicates a significant effect of mole-
cules and dye properties on the processes of dyeing the structure.

Conclusions

Thermal treatment is the reason for changes in the fibre structure, manifest-
ed by increased molecular coherence and deterioration of the overall internal orient-
ation of its matter.

The increase in molecular coherence is related to the formation of more intermo-
olecular bonds in which highly polar -CN groups are involved. The decrease in the overall orientation of the fibre studied is a consequence of the process of disori-
entation of macromolecules in the amor-
phous and mesomorphic matter.

Values of the sorption indexes are af-
fected both by the molecular and supra-
molecular structure of the fibre matter as well as by the physical and chemical characteristics of the dye molecule structure. The course of the process of diffusion of dyes inside the fibre depends on the mutual adjustment of the size and shape of their molecules and free microcapillary spaces in the fibre, as well as on interactions resulting from the electro-
static nature of chemical groups of dyes and fibre matter.

The biggest improvement in diffusion and sorption properties for all dyes test-
ed was obtained by subjecting the fibre to thermal pretreatment with steam and air at 220°C, which indicates that the use of appropriate thermal pre-treatment of PAN fibre contributes to a more effective dyeing process, leading to obvious eco-
nomic benefits.

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