

# THE EXAMINATION OF MOLECULAR AND SUPERMOLECULAR STRUCTURE CHANGES OF MAN-MADE CELLULOSE FIBRES UNDER THE INFLUENCE OF UV RADIATION

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## Abstract

*This paper presents research into the influence of UV radiation on the molecular and supermolecular structure of first-, second-, and third-generation manmade cellulose fibres, differing from each other in their initial structures and containing dulling agents.*

## Key words:

*Cellulose fibres, UV radiation, molecular structure, supermolecular structure*

## Introduction

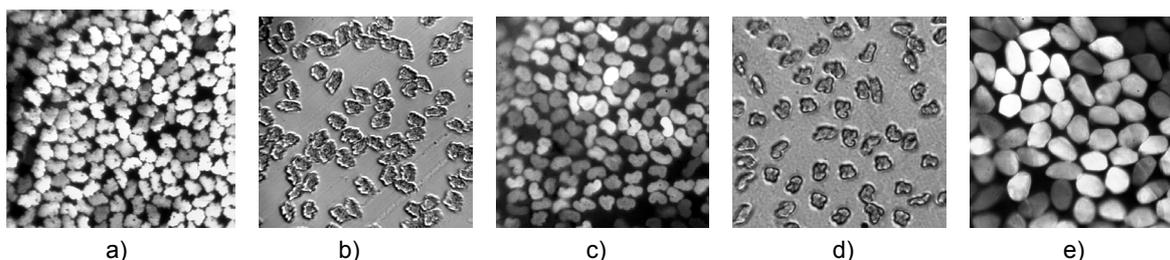
All textile products, especially woven fabrics and knitted fabrics that are meant for summer use under the influence of light, undergo a certain degree of weakening [1,2,3]. This is a result of the destruction of the fibres by the ageing process. The extent of the fibres' destruction clearly depends on the conditions of exposure. It also depends on the initial structure and its macroscopic characteristics [4]. In the case of cellulose man-made fibres, due to its initial structures (first-, second- or third-generation fibre), research into the influence of UV radiation on the transformation process of the fine structures seems to be justified [5].

## Measured materials

The test items included man-made cellulose fibres of different generations designated as 'bright' and 'dull', manufactured by Lenzing AG (Austria). The characteristics of the fibres tested are shown in Table 1. The images of the fibre cross sections are presented in Figure 1.

**Table 1.** Test material characteristics

Type of fibre	Metrological parameters	Shape of cross-section
Viscose standard 'bright'	(1,3dtex/39mm)	irregular
Viscose standard 'dull'	(1,3dtex/39mm)	irregular
Viscose modal 'bright'	(1,3dtex/39mm)	irregular
Viscose modal 'dull'	(1,3dtex/39mm)	irregular
Lyocell 'bright'	(1,3dtex/38mm)	oval alike



**Figure 1.** Images of the cross-section of: a) viscose standard fibres 'bright', b) viscose standard fibres 'dull', c) viscose modal fibres 'bright', d) viscose modal fibres 'dull', e) Lyocell fibres (a higher magnification was used due to the poor quality of the image)

## Measurement methods

The appropriately prepared fibre samples were exposed to UV radiation under artificial illumination conditions in a climatic chamber with a xenon tube as the source of radiation. The exposure of fibres to UV radiation was conducted in 8-hour cycles (at a relative humidity of  $\Phi=65\%$  and temperature of  $\vartheta=70^\circ\text{C}$ ) and 2 hours conditioning time under normal climatic conditions without irradiation (according to the manufacturer, a 24-hour exposure of samples to xenon tube radiation corresponds to 10 average days exposure to sunlight in a year). Changes in the fibre molecular and supermolecular structures were observed after 36, 72, 124 and 200 h of exposure. Samples were prepared and irradiated according to Polish standards PN-84 C-89018 [6].

The assessment of UV-induced changes in the molecular and supermolecular structures of fibres was based on the research results using the following three measurement methods [4]:

- IR absorption spectroscopy, allowing the evaluation of the fibre polymer at molecular and supermolecular levels;
- Determination of the fibre critical dissolution time, which assesses the molecular cohesion of polymer fibre matter; and
- Degree of swelling of fibres, giving as basis on which to interpret the changes which take place in the amorphous regions [7]

IR spectroscopic measurements of a specimen tablet preparation, comprised of 2 mg of powered fibre which was homogeneously dissipated in 200 mg of KBr, were carried out on a Shimadzu FTIR 8101M spectrophotometer. IR absorption spectra were recorded within the range of  $800\text{--}400\text{ cm}^{-1}$  in the systems  $T = f(1/\lambda)$ ,  $A = f(1/\lambda)$ , where T – transmission and A – absorption.

The spectrogram analysis was carried out in terms of changes in the absorption band intensity correlated with the characteristic functional groups of the given fibre polymer and changes in the intensity of the ‘crystalline band’, which was determined by the bands proposed by Dechant [8], as well as the internal standard band.

The quantitative analysis of the concentration of specified chemical groups was performed on the basis of Lambert-Beer’s law:

$$\ln \frac{I_0}{I} = \varepsilon \cdot c \cdot d \quad (1)$$

where:

- $I_0$  – the intensity of incident radiation;
- $I$  – the intensity of radiation after passing through matter;
- $\varepsilon$  – the molar coefficient of absorption;
- $c$  – the concentration of the absorbing groups;
- $d$  – the thickness of the absorbing layer.

The fibre crystalline index was found using the equations as proposed by Dechant [8]:

$$X_{IR} = E_{1315} / E_{1380}, \quad (2)$$

where:

- $X_{IR}$  – crystalline index of tested substance
- $E_{1315}$  – extinction absorbance band at wave number  $1315\text{ cm}^{-1}$
- $E_{1380}$  – extinction absorbance band at wave number  $1380\text{ cm}^{-1}$

The changes in the molecular coherence of the polymer were determined and analysed by measuring the critical time of fibre dissolution under a microscope with a Boethius heated base and polarised light. The fibres were dissolved at room temperature, in a solution composed of ammonia and Cuoxam at a ratio of 2:1.

In order to determine the degree of fibre swelling, changes in the dry and swollen fibre cross-section dimensions were analysed. Changes in the fibre thickness were measured with the help of a microscope at a magnification of  $600\times$ . An 18% solution of NaOH was used to swell the fibres. The degree of swelling was determined by the following relationship:

$$S_p = \left( \frac{d_{sp}}{d_s} - 1 \right) \cdot 100, \% \quad (3)$$

where:

- $d_{sp}$  – the average swelling of the fibre cross-section;
- $d_s$  – the average fibre cross-section;
- $S_p$  – the degree of cross-sectional fibre swelling [%].

## Test results

The 'crystalline' indexes as determined by the characteristics absorption bands of the tested fibres were tabulated as shown in Table 2. The critical dissolution times are listed in Table 3. The degrees of fibre swelling determined on the basis of fibre cross-sectional changes are shown in Table 4.

**Table 2.** Crystalline degree of man-made cellulose fibres of various generations

Type and symbol of fibre	Exposure time, hours	Crystallising degree, deg
Viscose standard 'bright'	0	0.36
	36	0.37
	72	0.38
	124	0.38
	200	0.39
Viscose standard 'dull'	0	0.33
	36	0.31
	72	0.30
	124	0.30
	200	0.31
Viscose modal 'bright'	0	0.35
	36	0.34
	72	0.32
	124	0.32
	200	0.35
Viscose modal 'dull'	0	0.35
	36	0.35
	72	0.34
	124	0.32
	200	0.34
Lyocell 'bright'	0	0.42
	36	0.42
	72	0.40
	124	0.36
	200	0.36

**Table 3.** Average dissolution time of man-made cellulose fibres t [s]

Type and symbol of fibre	Average dissolution time of initial fibre, s	Average dissolution time of fibers after exposure time, hours			
		36	72	124	200
Viscose standard 'bright'	29.2	34.9	36.5	39.0	42.7
Viscose standard 'dull'	32.9	38.5	45.5	46.3	50.4
Viscose modal 'bright'	31.8	38.0	38.4	38.1	39.1
Viscose modal 'dull'	43.9	45.8	46.8	47.8	48.4
Lyocell 'bright'	38.4	49.6	52.8	58.2	62.5

**Table 4.** Swelling degree values of cellulose fibres investigated

Type and symbol of fibre	Swelling degree of:									
	Viscose standard 'bright'		Viscose standard 'dull'		Viscose modal 'bright'		Viscose modal 'dull'		Lyocell 'bright'	
	0	200	0	200	0	200	0	200	0	200
Exposure time, hours	0	200	0	200	0	200	0	200	0	200
$d_s$	0.8	0.9	0.9	0.9	0.8	0.8	0.88	0.9	0.7	0.7
$d_{sp}$	2.0	1.9	2.3	1.9	2.0	2.3	2.2	2.2	1.5	1.7
$S_p$ [%]	165	111	156	111	150	188	150	144	114	143

## **Analysis of the tested fibres' molecular and supermolecular structure changes under the influence of UV radiation exposure**

### **Assessment of the fibre structure changes on the basis of IR spectroscopic measurements**

The intensity of the changes in the characteristic absorbance band testify to the changes in the fibres' molecular and supermolecular structure under UV radiation.

The decrease in the intensity of the absorbance of the band corresponding to the terminal units occurring at the macromolecular chain stem indicates the process of molecular degradation, proceeding randomly. The observed decrease in band intensity corresponding to the 1,4  $\beta$ -glycoside bands demonstrates that the macromolecular chain length is shortening (depolymerisation). The decrease in the absorbance band intensity, corresponding to the -C-C- group, confirms the glycoside ring opening.

The decrease in the absorbance band intensity corresponding to -OH indicates the possible transformation of these groups to aldehyde or carboxylic groups and the formation of new intermolecular bonding with the participation of these groups. The effect of this process is an increase in the polymer fibre molecular coherence, which is reflected by the increase in the critical dissolution time.

From the point of view of the supermolecular structure changes, the spectrogram analysis allows us to conclude that under the influence of UV radiation for standard and modal fibres the process of recrystallisation and decrystallisation does not take place. For Lyocell fibres, it can be seen that under long exposure times, the crystallinity index decreases.

### **Assessment of the fibre structure changes on the basis of the critical dissolution time measurement**

On the basis of the critical dissolution time values we obtained, it can be concluded that the UV radiation increases the molecular coherence of the fibres tested. This comes from the increase in the critical dissolution time values during the whole exposure cycle.

The smallest changes were observed for modal fibres, whereas the largest increase in KCR index was evident in Lyocell fibres. On the assumption that molecular coherence is determined by the intermolecular bonding (quantity and value of dissociation energy) in the fibre polymer, the results presented indicate an increase in the number of strong intermolecular bonds as a result of the transformation of molecular cellulose macromolecules.

### **Assessment of the fibre structure changes on the basis of degree of swelling**

The degree of swelling values of cellulose man-made fibres presented in Table 4 lead to the conclusion that exposure to UV radiation causes changes in the degree of fibre swelling. These changes occur at different levels of intensity for the different tested fibres.

- For viscose fibres 'bright' and 'dull', a decrease in degree of swelling can be observed.
- For the modal fibre 'dull', insignificant changes in the initial degree of swelling of fibre can be observed, as well as after exposure.

The results obtained agree with the results obtained with the KCR method, and above all confirm the polymer molecular transformation of the fibres tested:

- In the case of viscose fibres 'bright' and 'dull', the increase in strong intermolecular bonding causes a decrease in the degree of fibre swelling.
- In the case of modal fibres 'dull', only a small decrease in the degree of swelling of fibre was observed. The direction of changes, as can be judged, is caused by 'securing' of the fibrils by the dulling agent molecules present in the polymer fibre.
- In the case of modal 'bright' and Lyocel 'bright' fibres, an increase in the degree of swelling was observed. The cause of such a change in direction is the disintegration of the fibrils were joined by macromolecules, and the facilitation of penetration of the swelling agent molecules into the fibre interior.

## **Conclusion**

Upon the basis of the tests carried out, it can be concluded that UV radiation in the applied exposure conditions causes the polymer molecular and supermolecular structure in the investigated fibres to

change. The extent of these changes is clearly dependent on the initial fibre structure and the inserted additives.

- The least structure changes are observed in the case of modal fibres.
- The dulling agent added to the fibre polymer in the case of standard viscose fibres does not significantly influence the molecular and supermolecular structure changes of these fibres.
- Introducing dulling agents to modal fibres performs a protective role in protecting the polymer fibre from the unfavourable UV radiation effects.
- The Lyocell fibre structure, without any additives and under the given accepted exposure times to UV radiation clearly undergoes changes; these changes apply both to molecular and to the supermolecular structures.

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