

EXAMINATION OF THE AGEING OF SELECTED SYNTHETIC FIBRES UNDER THE INFLUENCE OF UV RADIATION

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Abstract

An attempt has been undertaken to assess the effect of UV radiation on the molecular and supermolecular structure of polyamide and polypropylene fibres that are characterised by various macroscopic features, colours and additives. Based on the measurements performed, the general conclusion can be drawn that UV radiation under the exposure conditions used in our experiments causes changes in both the molecular and supermolecular structures of the investigated fibres. The extent of these changes is clearly dependent on the initial fibre structure, the modifiers added and the macroscopic features.

Keywords:

Fibre ageing, UV radiation, molecular structure, supermolecular structure, crystallinity

1. Introduction

The growth of synthetic fibre manufacture has been accompanied by increasing requirements imposed on the manufacturers in respect of the fibres' physicochemical and physical properties, as well as the stability of these properties under the conditions of everyday use [1, 2]. Most fibres are subject to adverse effects of time or ageing, which are facilitated by the presence of UV radiation [3 - 6]. Fibre ageing results in polymer structural changes and consequently in some fibre properties [7 - 15]. The aim of this study is to explain the effect of UV radiation under artificial exposure conditions on structural changes in polyamide and polypropylene fibres by analysing the changes in molecular and supermolecular structures of these polymers.

2. Test items and scope of testing

The test items included continuous polyamide and polypropylene fibres with different degrees of dullness, colour and macroscopic features. Polyamide fibres had different cross-section shapes and delustrant contents, while polypropylene fibres with a circular cross-section differed in the drawing ratio, colour and the presence of UV absorber [16 -18]. The characteristics of the fibres used are given in Tables 1 and 2.

Prior to exposure, fibres were carefully combed and uniformly wrapped in parallel around elastic paper frames. The exposure of samples to UV radiation was carried out under artificial [insulation conditions in a 3001-type Feutron climatic chamber with a xenon tube as radiation source. According to the tube manufacturer, the exposure of samples to xenon tube radiation for 24 hours correspond to 10 average days in a year. The irradiation of fibres was performed in cycles: 8 hrs of exposure (at a relative humidity of 65% and temperature $T = 70^{\circ} \text{C}$) and 2 hrs of storage under standard conditions without irradiation. Changes to the fibre molecular and supermolecular structures were observed after 36, 72, 124 and 200 hrs of exposure. The sample preparation and irradiation process were carried out in accordance with Polish standard PN-84 C-89018.

Table 1. Characteristic of polyamide fibres

Type of fibre	Shape of cross-section	Thickness of fibre [µm]
<i>Polyamide 'dull'</i>	round	20.8
<i>Polyamide 'semi-dull'</i>	round	21.8
<i>Polyamide 'bright'</i>	round	21.2
<i>Polyamide 'bright'</i>	triangle	19.5

Table 2. Characteristic of polypropylene fibres

Type of fibre	Draw ratio	UV absorber	Thickness of fibre, µm
<i>Polypropylene 'bright' -natural colour</i>	5x	+	36.3
<i>Polypropylene 'bright' -natural colour</i>	7x	+	35.9
<i>Polypropylene -silver colour</i>	5x	-	35.5
<i>Polypropylene -black colour</i>	7x	+	36.6

3. Measurement methods

The assessment of UV-induced changes in the fibre molecular and supermolecular structures was based on three measurement methods: IR absorption spectroscopy, which allows one to evaluate the fibre polymer at the molecular and supermolecular levels; determination of the critical time of fibre dissolution, assessing the molecular cohesion of polymers, and the densitometric method, assessing the quantitative content of crystalline phase [13, 19].

The IR spectroscopic measurements were performed by means of a FTIR 8101M spectrophotometer from Shimadzu, using tablet specimens (2 mg of powdered fibre homogeneously dissipated in 200 mg of KBr). IR absorption spectra were recorded within the range 800-4000 cm⁻¹ in the systems $T = f(1/\lambda)$ and $A = f(1/\lambda)$. The spectrograms shown in Figures 1 and 2 for unirradiated fibres serve only to illustrate their character. The analysis of spectrograms was carried out in terms of changes in absorption band intensity correlated with the characteristic functional groups of the given fibre polymer (Tables 3 and 4), and changes in the crystallinity index determined from the bands proposed by Dechant [20], i.e. 'crystalline' bands and the internal standard bands. Examples of spectrograms are shown in Figures 1 and 2. The quantitative analysis of concentration ratio of specified chemical groups was performed on the basis of Lambert-Beer's law:

$$\ln \frac{I_0}{I} = \varepsilon c d$$

where:

I_0 – intensity of incident radiation

I – intensity of radiation after passing through matter

ε - molar coefficient of absorption

c – concentration ratio of absorbing groups

d – thickness of absorbing layer

The fibre crystallinity index was established using the equations as proposed by Dechant [20]:

- for polyamide fibre in the case of:

modification α - $x_{IR} = A_{i 1029} / A_{i 1075}$

modification γ - $x_{IR} = A_{i 977} / A_{i 1075}$

for polypropylene fibre: - $x_{IR} = A_{i 842} / A_{i 899}$

where:

x_{IR} – crystallinity index of the tested item

$A_{i 1029}$ - integral absorption of the band at wave number 1029 cm⁻¹

$A_{i 977}$ - integral absorption of the band at wave number 997 cm⁻¹

$A_{i 1075}$ - integral absorption of the band at wave number 1075 cm⁻¹

A_{1842} - integral absorption of the band at wave number 842 cm^{-1}
 A_{1899} - integral absorption of the band at wave number 899 cm^{-1}

Table 3. Polyamide 6 – Wave number band and kind of chemical groups in accordance with [19, 20]

α - modification	γ - modification	Type of vibration, Kind of chemical group
Wave number, cm^{-1}	Wave number, cm^{-1}	
3300	3300	ν (NH)
3200	3200	Resonans Fermi (Amide-I + Amide-II) z γ δ (CH ₂) (NH)
3091		Fermi's resonance : 2x Amide-II z γ (NH)
2936		γ_a (CH ₂)
2943		γ_s (CH ₂)
2868	2858	Amid I
1641	1647	Amid II
1545	1563	δ (CH ₂), N
1478		δ (CH ₂)
1464	1464	δ (CH ₂)
1452		δ (CH ₂), N- i CO-
1438	1441	δ (CH ₂), CO-
1316	1303	γ_w (CH ₂), γ_t (CH ₂), interaction with Amide III
1243	1236	Amid III
1266	1270	γ_t (CH ₂) lub γ (C α N)
1202		γ (CC)
1171	1172	γ (C α N)
1124	1122	γ (CC)
1075	1080	γ (CC)
1041	1030	γ (π , 0)
	1001	γ_0
1029		γ (π , π)
960		γ (0, π)
952		γ (CC)
929		γ_r (CH ₂), N- lub CO-
	917	γ_r (CH ₂)

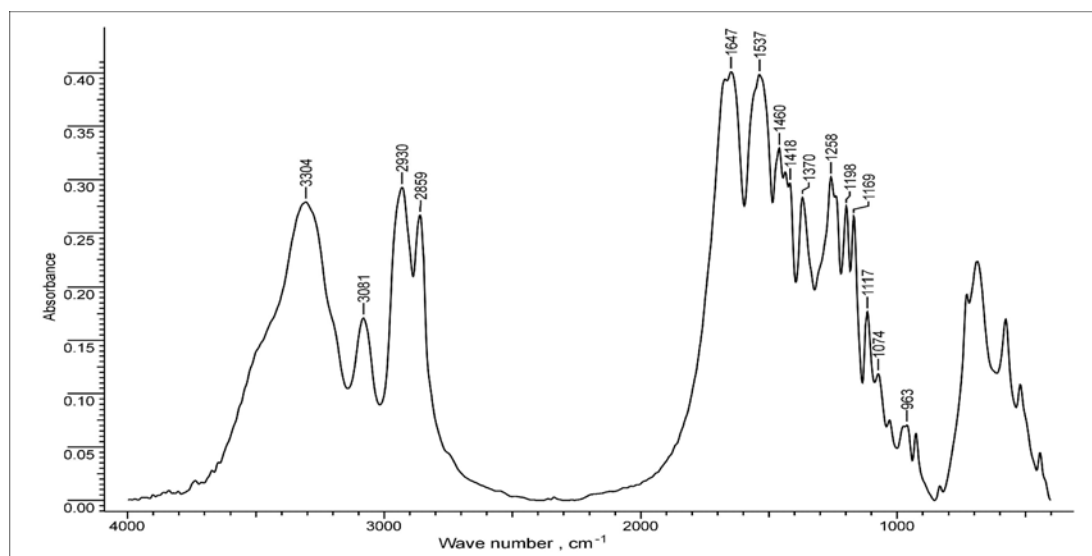


Figure 1. Spectrogram of unirradiated polyamide fibre „bright-round”

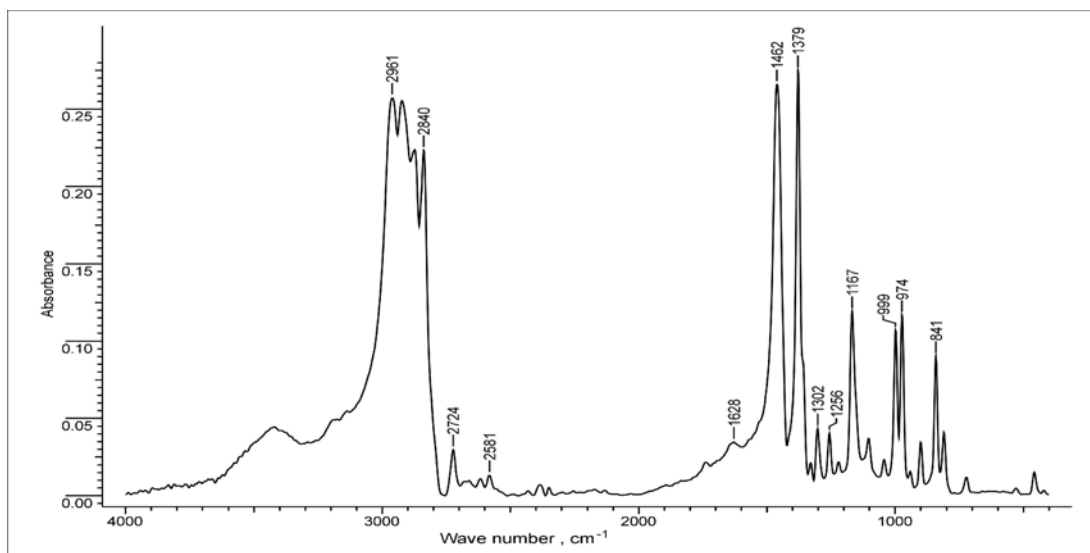


Figure 2. Spectrogram of unirradiated polypropylene fibre 'bright' - natural colour, draw ratio 5x

Table 4. Polypropylene – Wave number band and kind of chemical groups in accordance with [19, 20]

Isotactic	Syndiotactic	Type of vibration, Kind of chemical group
Wave number, cm ⁻¹	Wave number, cm ⁻¹	
	1463	$\bar{\delta}_a'$ (CH ₃)
	1462	$\bar{\delta}_a'$ (CH ₃)
	1461	$\bar{\delta}_a$ (CH ₃)
	1439	$\bar{\delta}_s$ (CH ₂)
	1436	$\bar{\delta}_s$ (CH ₂)
1378	1385	$\bar{\delta}_s$ (CH ₃)
1377	1386	$\bar{\delta}_s$ (CH ₃)
1365	1367	γ_w (CH ₂), $\bar{\delta}_s$ (CH ₃), $\bar{\delta}$ (CH)
1360	1365	γ_w (CH ₂), $\bar{\delta}_s$ (CH ₃), $\bar{\delta}$ (CH), γ_t (CH ₂)
1330	1344	γ_w (CH ₂), $\bar{\delta}$ (CH)
1326	1332	$\bar{\delta}$ (CH)
1304	1304	γ_w (CH ₂), γ_t (CH ₂), $\bar{\delta}$ (CH)
1296	1301	$\bar{\delta}$ (CH), γ_w (CH ₂)
1254	1264	γ_t (CH ₂), $\bar{\delta}$ (CH)
1220	1195	γ_t (CH ₂), $\bar{\delta}$ (CH), ν (C-C)
1168	1165	ν (C-C), γ_r (CH ₃)
1155	1166	ν (C-CH ₃), $\bar{\delta}$ (CH)
1103	1112	γ_r (CH ₃), ν (C-C)
1045	1051	ν (C-CH ₃), ν (C-C)
1034	1021	ν (C-CH ₃), γ_r (CH ₃), γ_t (CH ₂), $\bar{\delta}$ (CH)
998	996	γ_r (CH ₃), ν (C-CH ₃), $\bar{\delta}$ (CH), γ_t (CH ₂)
973	950	γ_r (CH ₃), ν (C-C)
941	930	γ_r (CH ₃), ν (C-C)
899	892	γ_r (CH ₃), γ_r (CH ₂), $\bar{\delta}$ (CH)
842	862	γ_r (CH ₃), ν (C-C)

The assessment of changes in the molecular coherence of polymer was performed by the physicochemical method of measuring the critical time of fibre dissolution under a microscope with a heated Boethius stage in a polarised light. Polyamide fibre samples were dissolved in a solution of phenol in tetrachloroethane with a weight ratio of 1:8, while those of polypropylene were dissolved in decalin.

The fibre's real density was determined by the densitometric method in a gradient column [21]. The fibre samples were placed in thermostated (at 25°C) gradient columns with known distributions of liquid density after previous deaeration (2 mm Hg for 20 min). After 24 h, the sample density was read off depending on the sample position in the gradient column. Then, the mass crystallinity degree was determined according to the following relationship:

$$x_d = \frac{[d - d_a] \cdot d_{cr}}{[d_{cr} - d_a] \cdot d}$$

assuming for polyamide fibres $d_{cr} = 1.174 \text{ [g/cm}^3\text{]}$; $d_a = 1.084 \text{ [g/cm}^3\text{]}$ [22]
and for propylene fibres $d_{cr} = 0.95 \text{ [g/cm}^3\text{]}$; $d_a = 0.85 \text{ [g/cm}^3\text{]}$ [23]

4. Results

Results of polyamide fibre ageing

The crystallinity degree x_{IR} calculated for characteristic bands is given in Table 5.

The values of critical time of dissolution are listed in Table 6 and those of real density of polyamide fibres are given in Table 7. The crystallinity index x_d calculated from the fibre real density is given in Table 8.

Table 5. Crystallinity degree of α - and γ - modification of polyamide fibres

Type of fibre	Time of irradiation, hrs	α - modification	γ - modification
<i>Polyamide 'dull'</i>	0	0.27	0.43
	36	0.31	0.37
	72	0.31	0.37
	124	0.35	0.35
	200	0.36	0.31
<i>Polyamide 'semi-dull'</i>	0	0.27	0.37
	36	0.35	0.36
	72	0.37	0.36
	124	0.44	0.35
	200	0.44	0.31
<i>Polyamide 'bright-round'</i>	0	0.40	0.29
	36	0.45	0.27
	72	0.45	0.27
	124	0.46	0.26
	200	0.48	0.23
<i>Polyamide 'bright-triangle'</i>	0	0.37	0.27
	36	0.37	0.27
	72	0.40	0.27
	124	0.40	0.26
	200	0.43	0.25

Tabela 6. Average time of polyamide fibres' dissolution t, s

Type of fibre	Unirradiated fibres	Time irradiation of fibres, hrs			
		36	72	124	200
<i>Polyamide 'dull-round'</i>	32.3	29.3	25.9	24.4	24.6
<i>Polyamide 'semidull-round'</i>	36.9	38.7	36.9	27.1	27.3
<i>Polyamide 'bright-round'</i>	35.9	37.8	31.2	29.3	31.4
<i>Polyamide 'bright-triangle'</i>	40.6	49.4	48.3	32.7	33.5

Table 7. Density of polyamide fibres d, g/dm³

Type of fibre	Unirradiated fibres	Time irradiation of fibres, hrs			
		36	72	124	200
<i>Polyamide 'dull-round'</i>	1.1353	1.1392	1.1396	1.1423	1.1428
<i>Polyamide 'semidull-round'</i>	1.1416	1.1418	1.1421	1.1424	1.1429
<i>Polyamide 'bright-round'</i>	1.141	1.142	1.1419	1.1422	1.1426
<i>Polyamide 'bright-triangle'</i>	1.1433	1.1436	1.1435	1.144	1.1453

Table 8. Crystallinity degree calculated from the fibres' real density

Type of fibre	Unirradiated fibres	Time irradiation of fibres, hrs			
		36	72	124	200
<i>Polyamide 'dull-round'</i>	0.59	0.63	0.64	0.67	0.67
<i>Polyamide 'semidull-round'</i>	0.66	0.66	0.66	0.67	0.67
<i>Polyamide 'bright-round'</i>	0.65	0.66	0.66	0.66	0.67
<i>Polyamide 'bright-triangle'</i>	0.68	0.68	0.68	0.68	0.70

Results of polypropylene fibre ageing

The fibre crystallinity degree calculated for characteristic bands is given in Table 9. The values of critical dissolution time of the irradiated polypropylene filaments are listed in Table 10. Table 11 contains the values of polypropylene fibre density. The crystallinity degrees of polypropylene fibres calculated from the obtained densities are given in Table 12.

Table 9. Crystallinity degree of polypropylene fibres

Type of fibre	Unirradiated fibres	Time irradiation of fibres, hrs			
		36	72	124	200
<i>Polypropylene 'bright' natural colour X=5x</i>	0.84	0.82	0.82	0.83	0.84
<i>Polypropylene 'bright' natural colour X=7x</i>	0.83	0.83	0.83	0.83	0.80
<i>Polypropylene-black colour X=5x</i>	0.76	0.80	0.80	0.81	0.85
<i>Polypropylene-silver colour X=7x</i>	0.85	0.85	0.87	0.89	0.91

Table 10. Average time of polypropylene fibres dissolution t, s

Type of fibre	Unirradiated fibres	Time irradiation of fibres, hrs			
		36	72	124	200
<i>Polypropylene 'bright' natural colour X=5x</i>	26.6	33.4	36.9	44.4	49.3
<i>Polypropylene 'bright' natural colour X=7x</i>	40.2	33.7	29.8	26.6	24.9
<i>Polypropylene black colour X=5x</i>	12.2	14.0	15.6	17.0	29.4
<i>Polypropylene silver colour X=7x</i>	38.6	38.1	39.4	43.8	86.1

Table 11. Density of polypropylene fibres d, g/dm³

Type of fibre	Unirradiated fibres	Time irradiation of fibres, hrs			
		36	72	124	200
<i>Polypropylene 'bright' natural colour X=5x</i>	0.9147	0.9161	0.9169	0.9172	0.9206
<i>Polypropylene 'bright' natural colour X=7x</i>	0.9153	0.9136	0.9121	0.9115	0.9112
<i>Polypropylene-black colour X=5x</i>	0.9212	0.9212	0.9212	0.9212	0.9214
<i>Polypropylene-silver colour X=7x</i>	0.9158	0.9156	0.9152	0.9154	0.9154

Table 12. Crystallinity degree calculated from the fibres' real density

Type of fibre	Unirradiated fibres	Time irradiation of fibres, hrs			
		36	72	124	200
<i>Polypropylene 'bright' natural colour X=5x</i>	0.67	0.68	0.69	0.70	0.73
<i>Polypropylene 'bright' natural colour X=7x</i>	0.68	0.66	0.66	0.65	0.64
<i>Polypropylene-black colour X=5x</i>	0.73	0.73	0.73	0.73	0.73
<i>Polypropylene-silver colour X=7x</i>	0.68	0.68	0.68	0.68	0.68

5. Discussion of results

Changes in the molecular and supermolecular structures of polyamide fibres under the influence of UV radiation

Assessment of fibre structure on the basis of IR spectroscopic measurements

The changes in the intensity of characteristic absorption bands indicate structural alterations in polyamide fibres due to UV irradiation. The decrease in the intensity of absorption bands correlated with the groups present in the macromolecular chain ($-\text{NH}-\text{CH}_2-$ $\lambda = 1169 \text{ cm}^{-1}$, $-\text{NH}-$ $\lambda = 3084 \text{ cm}^{-1}$ and $-\text{CO}-\text{NH}-$ $\lambda = 929 \text{ cm}^{-1}$, $\lambda = 1075 \text{ cm}^{-1}$, $\lambda = 1199 \text{ cm}^{-1}$) indicates that the process of molecular degradation proceeds in a statistically random way. The increase in the intensity of absorption bands correlated with the amine group $-\text{NH}_2-$ ($\lambda = 688 \text{ cm}^{-1}$) confirms the decomposition of macromolecule chains as shown by the increased number of end groups $-\text{NH}_2$. In semi-dull polyamide fibres, the changes in the intensity of absorption bands are observed in the initial stage of irradiation up to 36 h. Further exposure results in none or barely observable changes in the intensity of absorption bands. This may suggest that the molecular degradation of fibres proceeds to an insignificant extent and that the structure of macromolecules is stable.

The analysis of spectrograms in terms of changes in the supermolecular structure allows one to conclude that UV radiation causes a complex process of recrystallisation in fibres. Such a conclusion may be justified by the following facts:

- the changed positions of 'crystalline' bands in the obtained spectrograms indicates the rebuilding of the space lattice of the crystalline phase or the so-called crystallographic transformation that consists in the transformation of the γ -crystalline form (a hexagonal crystallographic system) into an α -crystalline form (a monoclinic crystallographic system);
- the increase in the intensity of absorption crystalline bands indicates that the degree of crystallinity is increased at the same time. The recrystallisation process proceeds most intensively in polyamide fibres containing a delustering agent.

Assessment of the changes in fibre structure on the basis of the critical time of dissolution

Based on the critical dissolution time data listed in Table 4, one can conclude that UV radiation actively modifies the molecular and supermolecular structures of the fibres under investigation. The effects of UV radiation are different in particular types of fibres, and can be interpreted as follows:

- the UV radiation-induced recrystallisation of fibres containing either a low quantity or no amount at all of delustrant causes the overall degree of crystallinity to increase with a simultaneous crystallographic rebuilding of the crystalline matter existing in initial fibres. The values of critical dissolution time increase first, and then decrease to a constant value. After 124 h of irradiation, the solubility deteriorates again;
- in the case of fibres with a higher content of delustering agent, the crystallographic transformation is the dominating process of recrystallisation. The values of critical dissolution time decrease up to 124 h of irradiation,; thereafter, the value of this index stabilises.

Changes in the molecular and supermolecular structures of polypropylene fibres due to UV radiation

Assessment of the changes in the molecular and supermolecular fibre structures on the basis of IR spectroscopic measurements

The changes in the characteristic absorption bands' intensity indicate structural changes in polypropylene fibres. From the IR spectroscopic measurement results, it follows that the effects of UV radiation on the supermolecular structure are different for particular types of fibres:

- in the case of polypropylene fibres dyed to black and silver colours, the recrystallisation process takes place, which can be confirmed by the increased intensity of absorption crystalline bands;
- in the polypropylene fibre with a fivefold draw ratio and a lustre surface, one can observe a slight decrease in the crystallinity degree after 36 h of irradiation. Further exposure causes the crystallinity to increase, so that after 200 h of irradiation the fibre reaches a crystallinity degree similar to that of an unirradiated fibre;
- the polypropylene fibre with a sevenfold draw ratio and a lustre surface shows a decreased intensity of the absorption crystalline band, which indicates decrystallisation.

Assessment of the changes in molecular cohesion on the basis of critical dissolution time

From the critical dissolution time data given in Table 8, it follows that UV radiation brings about changes in the molecular and supermolecular structures of the fibres under investigation. The effects of UV radiation are different in particular types of fibres, and can be interpreted as follows:

- the decrystallisation of polypropylene fibres with a sevenfold draw ratio and a lustre surface taking place under the influence of UV radiation results in a decreased overall degree of crystallinity,
- the UV irradiation of glossy polypropylene fibres with a natural colour and a fivefold draw ratio, as well as those dyed to black and silver colours, results in increased values of the critical dissolution time, which is accompanied by a distinct increase in the crystallinity degree as confirmed by IR spectroscopic measurements.

Assessment of the changes in the fibre structure on the basis of densitometric measurements

The analysis of the crystallinity degree data (Table 9) found on the basis of measuring the real density of the fibres under investigation allows one to conclude that the effects of UV radiation are different in particular types of fibres:

- the glossy polypropylene fibre with a natural colour and a fivefold draw ratio shows a slight increase in the degree of crystallinity during 200 h of irradiation,
- the glossy polypropylene fibre with a natural colour and a sevenfold draw ratio shows a slight decrease in the degree of crystallinity, while in black and silver polypropylene fibres, no changes in the degree of crystallinity were observed during 200 h of irradiation.

6. Conclusions

Based on the measurements performed, one can draw the following general conclusion: the UV radiation under the exposure conditions used brings about changes in both molecular and supermolecular structures of the fibres under investigation. The extent of these changes is clearly dependent on the initial fibre structure, added modifiers and macroscopic features. In detailed terms, the following conclusion can be drawn:

- polyamide fibres

- The structure of standard fibres without any additives is subject to changes under the influence of UV radiation within the exposure time used. The changes concern the molecular and supermolecular structures, and are revealed after a longer time of exposure.
- A low addition of a delustering agent to the fibre-forming polymer protects the fibre considerably against the process of molecular and supermolecular rebuilding. Slight changes are observed in fibres irradiated within the shortest time, and these remain at a constant level even upon prolonging the time of exposure.
- A high addition of the delustering agent to the fibre polymer intensifies both the molecular and supermolecular structure's rebuilding.
- The presence of the delustering agent in the fibre gives rise to an intensive crystallographic transformation and an increase in the overall degree of crystallinity in proportion to the exposure time.
- The shape of the fibre cross-section affects the intensity of changes in fibre structure under the influence of UV radiation. In the case of fibres with a triangular cross-section, smaller changes are observed than in fibres with a circular cross-section.

- polypropylene fibres

- Polypropylene fibres with various draw ratios, and consequently with various thicknesses when exposed to UV radiation, behave almost in the same way –there are practically no changes in the degree of crystallinity.
- The increase in the draw ratio of polypropylene fibres intensifies the process of structural changes, which result in chain decomposition.
- The addition of a UV absorber and a black dye into fibres noticeably prevents the adverse molecular rebuilding of the fibre polymer.
- A silver dye added to the fibre containing no UV absorber protects the fibre polymer against the adverse effects of UV radiation. Only prolonged exposure to UV radiation brings about an intensive change in the molecular fibre structure and an increase in the degree of crystallinity.

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