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Influence of the structures of polyamide 6 fibers on their ageing under intensive insolation conditions

Summary — The effects of large doses of UV radiation, relating to actual operational use during 1, 2 or 5 summer seasons, on changes of chemical structures, crystalline structures, morphology and tensile properties of four types of polyamide 6 were investigated. The fibers differed in cross-section shape and mat degree caused by TiO_2 addition. The fibers were tested using, among others, SEM and IR methods. Critical dissolution time (CDT) was also investigated.

Key words: polyamide 6, fibers, ageing, chemical structure, crystalline structure, morphology, tensile properties.

WPŁYW STRUKTURY WŁÓKIEN Z POLIAMIDU 6 NA PRZEBIEG ICH STARZENIA W WARUNKACH SILNEGO NASŁONECZNIENIA

Streszczenie — Zbadano wpływ naświetlania dużymi dawkami promieniowania UV (odpowiadającego rzeczywistemu użytkowaniu w ciągu 1, 2 lub 5 sezonów letnich) na zmiany budowy chemicznej, charakteru struktury krystalicznej (tabela 4) i morfologii oraz właściwości mechanicznych przy rozciąganiu (tabela 5) czterech rodzajów włókien z poliamidu 6 różniących się kształtem przekroju oraz — spowodowanym dodatkiem TiO_2 — stopniem zmętnienia (tabela 1). Posługiwano się przy tym metodami SEM (rys. 1—4) i IR (tabela 2) a także pomiarem krytycznego czasu rozpuszczania (CDT, tabela 3).

Słowa kluczowe: poliamid 6, włókna, starzenie, budowa chemiczna, struktura krystaliczna, morfologia, właściwości mechaniczne przy rozciąganiu.

Polyamide fibers are widely used in many fields, often under different weather conditions. Therefore, it is important to examine the influence of natural climatic conditions such as insolation or effects of heat, moisture and oxygen on the structures and properties of these fibers. Polyamide fibers are sensitive to light, especially at wavelength within UV range. Under the influence of light the fiber-forming polymer undergoes a destruction by means of photolysis and photooxidation. These processes, generally known as "ageing", result in the deterioration of processing and performance properties of polyamide fibers. Sometimes these processes can result even in a total fiber destruction [1—5].

Our research described in this paper were focused on finding of the effects of various microscopic polyamide 6 fibers features and variable content of TiO_2 in these fibers on their ageing after exposure to UV radiation.

EXPERIMENTAL

Materials and samples preparation

Undyed polyamide 6 fibers, produced by Stilon plant in Poland, with various contents of delustrant (TiO_2) and variable cross-section shapes were tested. The characteristics of the fibers is given in Table 1. The preparation of fiber samples for the ageing process consisted in placing them on specially made elastic frames.

Table 1. Characteristics of the fibers used

Fiber type	Cross-section shape	Fiber thickness, μm
Polyamide 6 fiber "dull"	round	20.8
Polyamide 6 fiber "semi-dull"	round	21.8
Polyamide 6 fiber "bright"	round	21.2
Polyamide 6 fiber "bright"	triangle	19.5 (side length)

Irradiation

The ageing process under the influence of UV radiation under conditions corresponding to intensive insolation was carried out with the use of a quartz lamp (type L6/58, 375W). The irradiation of fibers was performed in cycles including exposure for 20 min and exposure stoppage for 15 min. The exposure time 40 min under the conditions used corresponds to one-season exposure of a

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textile fabric to sunlight during the summer period, *i.e.* about 200 h. It was found previously that the exposure to UV for such period of time resulted in the fading of a reference sample in the 4 blue scale used for testing colour fastness to light.

Samples were irradiated in cycles using a number of cycles corresponding to 200, 400 and 1000 h of real exposure to sunlight (1, 2 and 5 summer seasons), satisfying approximately the requirements of PN-EN ISO 105-B06: 2004.

Test methods

The assessment of changes in the polyamide fiber structure due to UV irradiation was made on the basis of the results obtained with the use of the following methods:

— IR absorption spectroscopy to assess the changes in polymer at molecular and supermolecular levels,

— critical dissolution time method (CDT) to assess the changes in the molecular coherence of polymer and

— scanning electron microscopy (SEM) to examine the morphology and superstructure (including fiber cross-section and fracture surfaces), especially fibrils and spherulites.

Additionally, the mechanical properties of the exposed fibers were assessed on the basis of the stress-strain curves.

IR spectroscopic measurements

IR analysis was carried out by the transilluminating technique using tablet specimens containing 1 % of powdered fiber. IR absorption spectra were recorded within the wavelength range from 4000 cm^{-1} to 400 cm^{-1}, in the following systems: $T = f(1/\lambda)$, $A = f(1/\lambda)$. The analyses of spectrograms were carried out in terms of changes in corrected absorption for absorption bands at wave number values: 696 cm^{-1}, 1030 cm^{-1} and 1119 cm^{-1}, relating to the chemical groups: $-NH_2$, -CONH- and -C-C-, respectively. The changes in the crystallinity index values were determined from so-called crystalline absorption bands and the bands of internal standard.

The values of fiber crystallinity index $x_{IR\alpha}$ were calculated using Dechant's formulas [6], namely for modification α $x_{IR\alpha} = A_{i1030}/A_{i1074}$, and for modification γ $x_{IR\gamma} = A_{i976}/A_{i1074}$ where: $x_{IR\alpha}$, $x_{IR\gamma}$ — examined indices of crystallinity for crystallographic forms α and γ and A_{i1030}, A_{i976}, A_{i1074} — integral absorptions of the bands at wave number values 1030 cm^{-1}, 976 cm^{-1} and 1074 cm^{-1}, respectively.

CDT method

According to this method the process of fiber dissolution in phenol:tetrachloroethane mixture (1:20 by wt.) at temp. 23.5 °C was observed under a microscope. The determined CDT value for each measurement variant was a mean value of 15 measurements.

SEM method

The microscopic observations were made with the use of a secondary electron detector (photomultiplier + scintillator) under a high vacuum (10^{-4} Pa). The images were recorded with the use of digital Semafore system.

Mechanical properties

Breaking stress, relative elongation at break and initial tensile modulus were measured according to standard PN-EN ISO 5079:1999 using the tensile Instron type 4402.

RESULTS AND DISCUSSION

Changes in fiber molecular structure

Results of IR spectroscopy

The changes in polyamide fiber molecular structure due to exposure to UV radiation are confirmed by: reduction in the intensity of absorption bands relating to -CONH- and -C-C- groups in the macromolecule chain at wave number values: 1030 cm^{-1} and 1119 cm^{-1}, and increase in the intensity of bands which relate to end groups $-NH_2$ at wave number value: 696 cm^{-1}, indicating statistically random chain disintegration (Table 2).

Table 2. Values of corrected absorbance of absorption bands: 696 cm^{-1}, 1030 cm^{-1}, 1119 cm^{-1} relating to chemical groups: $-NH_2$, -CONH- and -C-C- in PA6 fibers

Fiber type (see Table 1)	Exposure time (number of summer seasons)	Corrected absorbance for absorption bands		
		696 cm^{-1} $-NH_2-$	1030 cm^{-1} -CONH-	1119 cm^{-1} -C-C-
Polyamide fiber round-"bright"	0	0.69	0.09	0.35
	1	0.68	0.09	0.36
	2	0.65	0.08	0.34
	5	0.70	0.10	0.40
Polyamide fiber round-"semi-dull"	0	0.37	0.10	0.39
	1	0.37	0.09	0.39
	2	0.37	0.10	0.35
	5	0.36	0.09	0.35
Polyamide fiber round-"dull"	0	0.71	0.10	0.37
	1	0.73	0.09	0.38
	2	0.74	0.09	0.40
	5	0.71	0.09	0.38
Polyamide fiber triangle-"bright"	0	0.41	0.09	0.40
	1	0.72	0.10	0.39
	2	0.70	0.10	0.36
	5	0.66	0.07	0.33

Measurements of critical dissolution time

The most significant changes in CDT values (Table 3) can be observed in initial fibers and fibers exposed to UV radiation for a period corresponding to first 200 h exposure (1 season). Fibers containing either no or low quantity of delustrant, denoted as round "bright", round "semi-dull" and triangle "bright" show a clear reduction in CDT after exposure for the longest time used. In the case of fibers round "dull", the presence of TiO_2 accelerates the photolysis process during the initial stage of exposure (one and two seasons), however its presence in fiber clearly restricts the effects of photolysis during prolonged exposure of the fiber to light.

Table 3. Average dissolution time of the examined polyamide fibers

Fiber type (see Table 1)	*CDT* value, s			
	Exposure time (number of summer seasons)			
	0	1	2	5
Polyamide fiber round-"bright"	20.2	15.2	15.1	11.1
Polyamide fiber round-"semi-dull"	15.2	12.1	11.9	10.0
Polyamide fibers round-"dull"	21.5	12.5	10.5	10.0
Polyamide fiber triangle-"bright"	13.7	13.1	13.0	10.8

In the case of polyamide fibers with a triangular cross-section, there is no significant change in CDT during the initial stage of exposure; only the prolonged exposure to UV radiation causes decrease in CDT index to. This seems to be due to the different character of light incidence against a flat surface with triangular cross-section as compared to the fibers with circular cross-section. Due to the partial reflection of radiation from the flat fiber surface a considerably lower dose of UV rays is absorbed than in the case of fibers with a round cross-section.

Changes in fiber supermolecular structure

Table 4 shows the results of assessment of the changes in supermolecular structure of the fiber-forming polyamides based on the changes in crystallinity indices $x_{IR\alpha}$ and $x_{IR\gamma}$. These data characterize the fractions of crystallographic modifications α and γ in polyamide fibers *versus* exposure time.

So, one can conclude that recrystallisation process takes place in the fibers under the influence of UV radiation, namely so-called crystallographic transformation or the reconstruction of crystallographic lattice from modification alfa (α) into gamma (γ) type modification.

In the case of polyamide fiber round "semi-dull", the fraction of crystallographic form γ increases during the initial stage of exposure, while the fraction of a form is decreased. This indicates the crystallographic transformation of more ordered modification a into modification γ with a lower degree of order. When the exposure time is prolonged the fraction of crystallographic form γ clearly decreases, while the fraction of modification a decreases only to a slight extent. The most serious decrease in the total crystallinity index x_{IR} is observed for polyamide fibers round "bright" and round "semi-dull". Clearly lower changes of this index are observed in mat fibers of round cross-section. In these fibers one can observe the clearest process of transformation of crystallographic modification α into modification α. The fibers showing triangular cross-sections do not show such drastic changes in crystallinity due to the exposure to UV radiation.

Table 4. Fractions of crystallographic modifications α- and γ- in PA6 fibers

Fiber type (see Table 1)	Exposure time (number of summer seasons)	Modification α [-]	Modification γ [-]
Polyamide fiber round-"bright"	0	0.27	0.42
	1	0.28	0.33
	2	0.26	0.37
	5	0.25	0.33
Polyamide fiber round-"semi-dull"	0	0.28	0.41
	1	0.24	0.47
	2	0.27	0.34
	5	0.25	0.20
Polyamide fibers round-"dull"	0	0.26	0.32
	1	0.22	0.26
	2	0.17	0.27
	5	0.19	0.35
Polyamide fiber triangle-"bright"	0	0.23	0.29
	1	0.24	0.27
	2	0.25	0.28
	5	0.27	0.28

Changes in fiber morphological structure

The SEM images of exposed polyamide fibers show clear changes in morphological structures of fiber surfaces and interiors (Fig. 1—4). The most intensive changes in fiber surface were observed in glossy ("bright") fibers with a round cross-section, revealed as a distinct carving effect with no clearly marked direction (Fig. 1b). Such a curving effect in mat fibers is less visible than in glossy ones, being directed across the fiber axis. In fibers with triangular cross-sections, the curving effect is of a finer character, being outlined at some angle to the fiber axis (Fig. 4b).

On the fractures of the exposed fibers one can observe a separation of fibrillar structures. The most intensive changes appear in "bright" fibers, especially those with a triangular cross-sections and they correspond to the direction of surface curving. In the case of mat fibers with a round cross-sections, one can observe a separation into the structures of smaller dimensions.

Mechanical properties of the fibers

The results of testing of some mechanical properties of the examined fibers after exposure (breaking stress, elongation at break and initial modulus values) are given in Table 5.

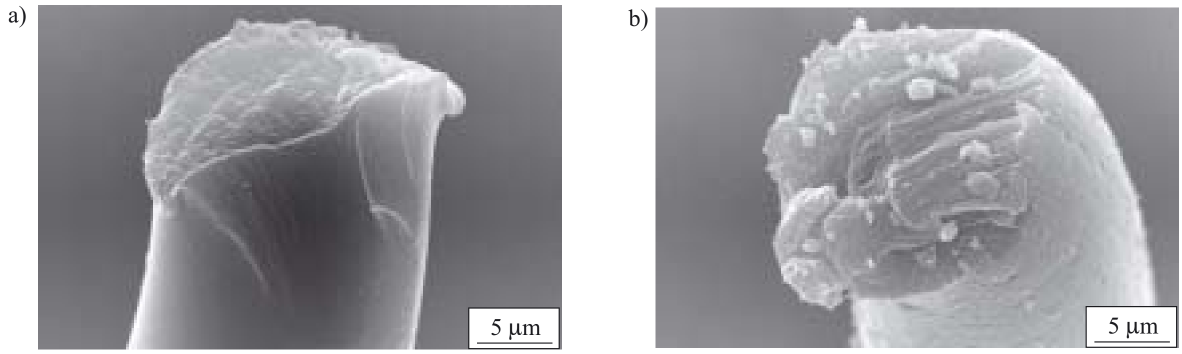

Fig. 1. SEM images of a fiber round-"bright": a) initial, b) after exposure for 5 seasons

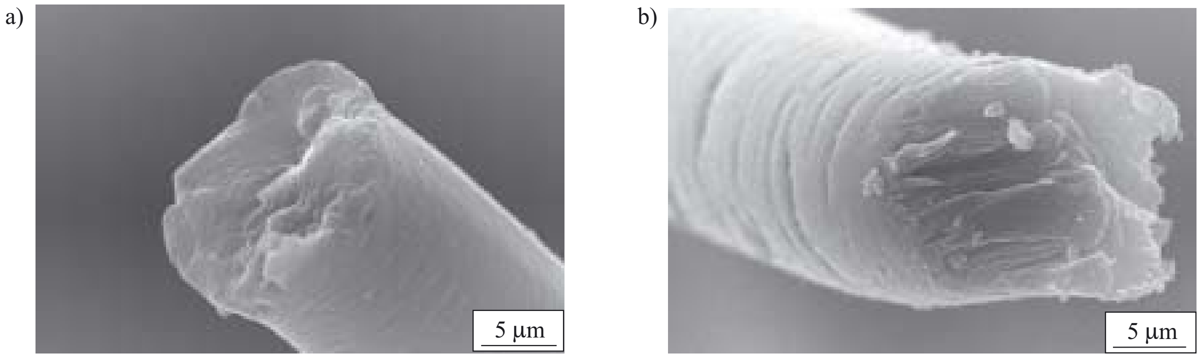

Fig. 2. SEM images of a fiber round-"semi-dull": a) initial, b) after exposure for 5 seasons

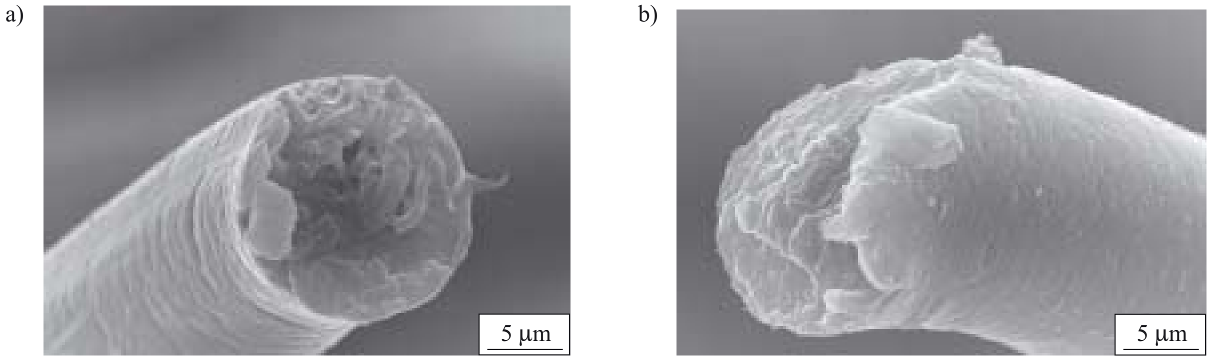

Fig. 3. SEM images of a fiber round-"dull": a) initial, b) after exposure for 2 seasons

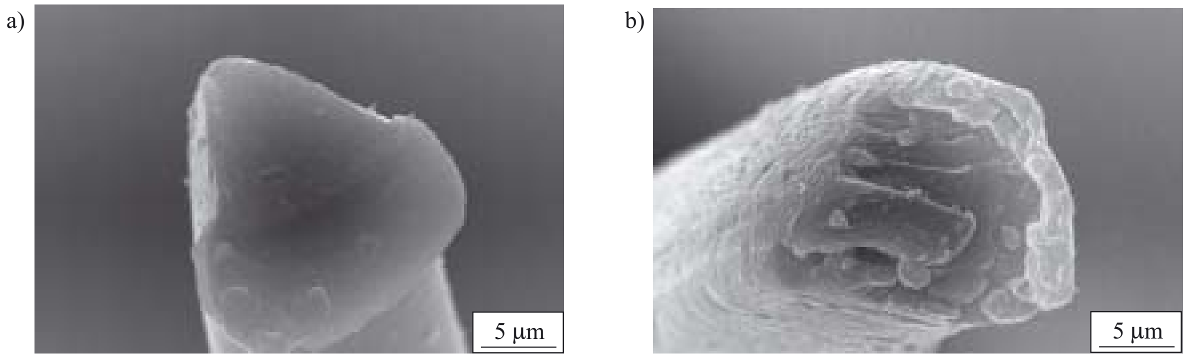

Fig. 4. SEM images of a fiber triangle-"bright": a) initial, b) after exposure for 5 seasons

It is clear that the exposure process brings the distinct changes in the examined parameters. The tenacity (σ_b values) of fibers decreases with increasing time of exposure. The greatest reduction in tenacity is observed in "bright" fibers with triangular cross-sections amounting to about 35 % of the initial values, while the tenacity of "bright" fiber with round cross-section decreased by about 20 % and that of "dull" fibers with round cross-

-sections — only by about 5 %. An increase in exposure time is accompanied also by the decrease in total deformation of fibers. The greatest changes of ε_b are observed also in "bright" fibers with triangular cross-sections, with the decrease amounting to about 70 % and in "bright" fibers with round cross-sections showing a decrease of about 50 %, while the smallest decrease in this modulus (about 25 %) took place in "dull" fibers with round cross-sections. The changes in tensile modulus were not so pronounced.

Table 5. Changes in mechanical properties polyamide fibers under the influence of UV exposure

Fiber type, exposure time (number of summer seasons)	Breaking stress σ_b cN/tex	Relative elongation at break ε_b, %	Initial tensile modulus M cN/tex
polyamide fiber round-"bright"			
0	48.9	58.3	279.2
1	44.9	37.7	327.7
2	41.6	31.2	321.5
5	40.8	29.0	340.4
polyamide fiber round-"semi-dull"			
0	42.2	72.7	205.8
1	38.8	57.6	236.5
2	38.8	51.2	229.4
5	36.6	42.6	240.7
polyamide fiber round-"dull"			
0	41.7	57.6	232.5
1	40.4	51.4	257.2
2	37.1	40.7	259.7
5	39.5	46.0	255.5
polyamide fiber triangle-"bright"			
0	43.3	60.3	242.5
1	41.9	54.2	262.6
2	34.0	30.8	241.3
5	28.3	20.2	229.1

Thus, the shape of cross-section significantly influences the fiber mechanical properties. In the fibers with triangular cross-sections one can clearly observe more substantial decrease in breaking stress and decidedly greater change in elongation at break as compared to those for the fibers with round cross-sections.

CONCLUSIONS

Based on the results of the tests performed with polyamide (PA6) fibers with various contents of delustrant (TiO_2) and different macroscopic features, one can see that UV radiation causes fiber ageing, and the effect of ageing intensifies with the prolongation of fiber exposure to UV radiation, resulting in changes in the molecular, supermolecular and morphological structures of the fibers as well as in changes of their mechanical properties.

The more details conclusions are as follows:

— As far as the molecular structure is concerned, the exposure of fibers to UV radiation leads to molecular destruction of the fiber-forming polymer as confirmed by IR spectra obtained: they show increased number of end groups and decreased number of groups -CONH- and -C-C- in the polymer chain. The direction and intensity of the destruction strictly depend on the delustrant content and on the macroscopic features of the fibers. Fibers with triangular cross-sections show higher resistance to photolysis than those with round cross-sections. An addition of delustrant (TiO_2) accelerates the polymer photolysis at the initial stage of exposure. However, after a prolonged exposure to light, the presence of TiO_2 in fibers limits the adverse effects of photolysis. This is confirmed also by the direction of changes in mechanical properties which become relatively slightly deteriorated.

— What concerns the supermolecular structure, the exposure of fibers to UV radiation causes a decrease in the fiber crystallinity degree, while the crystallographic lattice is transformed from modification α into γ. The intensity of these processes depends on the delustrant content as well as on the fibers macroscopic features. The crystallographic transformation is most pronounced in the fibers containing a delustrant. In the case of fibers with triangular cross-sections, no significant in crystallinity changes were observed after the exposure to UV radiation.

— As far as the morphological structure is concerned, the exposure of fibers to UV damages their surfaces, revealed as a strong curving effect and volumetric changes in the form of separated fibrillar structures inside the fibers. These changes are particularly visible in glossy fibers.

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Received 15 IX 2008.