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Impact of Activator Content on the Process of Photodegradation of PP Non-Wovens

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Abstract

The paper presents the test results of non-wovens modified by an activator in different concentrations, produced by the spun bonding method. The aim of the research was to assess the photodegradation process of modified PP non-wovens in dependence on the selected concentration of the modifying agent in the fibre mass and the possibility of introducing a new range of PP non-wovens in agriculture. Non-wovens having a mass per unit area of 100 g/m² were exposed to sunlight during its highest intensity for a period of four months, and UV irradiance was tested in a xenon lamp with radiation doses corresponding to exposure to sunlight. The samples were exposed to the same energy value of visible and UV radiation in a given series of exposure. For the variants of non-wovens tested, the tensile strength and mass per unit area were tested and the surface topography of the non-wovens analysed. Microscopic analysis of fibre damage in the modified non-wovens was carried out after different degrees of exposure to light. It was observed that PP non-woven samples exposed outdoors degraded more intensively than those tested in the Xenotest.

Key words: photodegradation, polypropylene nonwoven, PP with activator.

Introduction

For many years it has been believed that the advantages of products made of synthetic polymers are: durability and resistance to physical and chemical factors. This feature is the reason for the accumulation of enormous amounts of waste which, without natural decomposition, pollutes the environment. A small portion of it is recycled. Currently, the aim is to obtain synthetic materials that are decomposed under the influence of natural factors. However, these must be materials of define decomposition time, and the conditions under which decomposition occurs are controlled. Research is being carried out to obtain biodegradable products [1-3]. Products with a low starch content of up to 15% are usually agricultural films, compostable waste bags, disposable packaging, and personal care articles [4-5]. Photodegradable films are already being used in agriculture to protect sowings or accelerate plant vegetation. After fulfilling their task, they decompose under the influence of light and do not need to be removed. The sensitivity of polypropylene (PP) to UV light can be an advantage in products which, after fulfilling their function, should decompose without additional disposal outlays, if possible. PP fibres are relatively resistant to temperature, but oxidise in a relatively easy manner at elevated temperatures. Research on the protection of polypropylene and, in particular, PP fibres, was carried out already in the 1960s [6] and continued along with the development of directions concerning the modification of polymers [7, 8]. The fibres degrade

under the influence of sunlight. Degradation in the surface zone of the fibre (up to 1 µm) occurs within (100-150 h) of xenon lamp exposure. Exposure to light for over 200 h causes oxidation of the fibre interior. Fibres behave similarly in sunlight. Based on microscopic observation of car seat fabrics after 5 years of use, Barish [9] found fibre fractures reaching to the core. According to Blais, Carlson, Clark and Sturgeon [10], the photooxidation of PP fibres under the influence of xenon lamp light causes first a decrease in breaking elongation and then a reduction in strength. Observations using electron microscopy have shown that short-wave solar radiation causes transverse fractures in the fibres. Carlson, Clark and Wiles studied the chemical changes and deterioration of mechanical properties [11] as well physical and microstructural changes caused by the photooxidation of PP fibres. Rabello and White [12, 13] showed that the mechanical properties of degraded PP depend not only on the degree of chemical degradation but also on the physical structure of the polymer. Many studies, discussed in detail by Carlson and Wiles [14] and Barish [9], focused on the problem of PP stabilization to light exposure. Several studies have been carried out on the light resistance of dyed PP fibres [15], the influence of pigments for dyeing on the progression of photooxidative degradation and the influence of stabilizers on the strength of PP fibres dyed with various pigments [16]. Osaka, Kobayashi and Kayano studied the effect of a series of transition metal (Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn) stearates on retarding photo-degradation

Table 1. Intervals of exposure time and doses of solar and UV radiation for modified PP non-wovens.

Series (two weeks)	Energy (dose) of radiation in each series, kJ/m ²	Radiation energy (dose) (increasing) kJ/m ²
I	2569	I 2 569
II	6370	I+II 8 939
III	6315	I + III 15 253
IV	8549	I + IV 23 800
V	8715	I + V 32 515
VI	8794	I+VI 41 309
VII	8268	I+VII 49 578
VIII	8031	I+VIII 57 608

Table 2. Conditions of the light exposure of modified PP non-wovens in the Xenotest Alpha HE.

Test conditions	I Without rain phase	II Phase with rain /0 l/min
Time of one exposure cycle, min	30	
Duration of phase in the exposure cycle, min	29	1
Rotation of sample holders	No turnover	
Study time, h	Variable in dependence on the intensity of UV radiation of daylight in the appropriate series	
Radiation energy, W/m ²	60	60
Temperature BST, °C	60	50
Temperature CHT, °C	40	35
Air humidity, %	40	100 (rain)
Filter	Xenochrome 300	

and observed that PP degradation is accelerated by vanadium, iron and titanium stearates, retarded by copper stearate, and that the other stearates had no appreciable effect [17]. Later research showed that the degradation properties of the widely used polymer polypropylene (PP) can be improved by integration with cobalt stearate (CoSt₂) and iron stearate (FeSt₃) as prooxidants with accelerating weathering degradation [18]. Studies by Schmidt, Ratajska, Brzezińska and Twarowska-Schmidt [19÷21] on the influence of pigments on the resistance of PP fibres to light showed that pigments often have a catalyst effect on PP photooxidation. There are products made of PP fibres that are designed for outdoor use and are resistant to sunlight during 10 years of exposure under natural conditions in a moderate climate. The agricultural industry has diverse needs and requirements for vegetables, fruits and flowers in relation to the environment and limited opportunities to ensure effective plant protection against diseases and pests. Farmers are looking for solutions that would enable the cultivation of crops with due care for the environment. Weed control in organic vegetable cultivation is one of the most labour intensive and expensive agricultural procedures as it is not possible to use herbicides here. To reduce weed infestation, mulching with black film, non-woven or organic mulch of plant origin,

such as straw or mowed aerial parts of grass and plant mixtures, are used [22]. The use of polypropylene non-woven coverings in early vegetable cultivation results in a significant reduction of losses caused by pests foraging on the root system or damaging the leaves and stems of plants. Mulching with non-wovens reduces weed infestation in plant cultivation and eliminates weeding. The use of non-woven coverings improves plant growth conditions and contributes to their much better development [23, 24].

In this paper, the authors focused on the analysis of photodegradation by assessing the fibre strength and morphology changes in modified PP non-wovens following their exposure to sunlight and xenon lamp light.

Materials and methods

As the test object the authors selected PP non-wovens with a mass per unit area of 100 g/m² and modified with iron stearate in different percentages: A – 0.02%, B – 0.05%, C – 0.1%, D – 0.3% and a non-woven without the addition of an activator, marked as a blank sample (0). It was assumed to perform the experiment in the spring and summer period, i.e. when the greatest sun exposure occurs. The total exposure time of non-wovens to sunlight was 16 weeks. A stand for the outdoor

exposure of samples was built. Samples sized 15 x 150 mm were prepared for testing under sunlight on Xenotest apparatus. The exposure of samples to visible and UV radiation was carried out until they were destroyed (photodegraded). Weather conditions and light intensity were measured with CMP 3 radiation sensors – in the scope of UV-VIS (310 ÷ 2800 nm) and with CUV 4 radiation sensors – in the scope of UV (305 ÷ 385 nm). The sensors can operate in the temperature range of -40 °C to +80 °C and are weather resistant. They operate at low voltages of (0-20 mV) and collect data every 30 s, while recording and archiving the energy of UV and visible radiation. They are designed for use both outdoors and indoors. Data recorded by the sensors were transmitted and recorded by LogBox SD – an 8-channel device that allows the simultaneous connection of several instruments. Each channel has the ability to record data and convert them to the values and units required. The collection of metrological parameters requires the use of sensors and LogBox together. LogBox SD has software for self-configuration, and the parameters of Kipp & Zonen radiometers are predefined, with the output to RS 232 communication port being provided with an internal memory of 128 kB and a 512 MB SD memory card for recording. The results were recorded at intervals of 2 weeks.

The daily integral P was calculated from **Equation (1)**:

$$P = \frac{24 \cdot 3,6 \cdot \sum W}{N} \text{ kJ/m}^2 \quad (1)$$

where:

P – radiation dose, kJ/m²,
W – radiation energy, W/m²,
n – number of measurements per day.

The non-wovens were tested in artificial light on an Xenotest ALPHA HE device by Atlas with a water-cooled xenon arc lamp at a power of 2 200 W. To simulate daylight outdoors, Xenochrome 300 filters and an external cylinder made of Suprax glass were used. The sensors measured and regulated the chamber temperature (CHT) and black standard temperature (BST), programmed by the energy value read from the CUV4 sensor during the adopted time of exposure under natural conditions. After each stage of testing, which was a multiple of two weeks, two sets of samples were obtained (tested under natural conditions and using the Xenotest apparatus).

For the samples concerned, the mass per unit area and specific strength were determined. A Zwick Strength Testing Machine was used for strength testing with a constant increase in elongation, type CRE, and with a 1 kN load capacity head. Flat clamps covered with rubber were used to prevent the destruction of samples between the clamps.

The surface topography of non-wovens was investigated using a JSM-35C scanning electron microscope by JOEL at a resolution of 6 nm and Jeol Gold Coating apparatus, type JFC-1100 “FINE COAT”. ORION 6 software was used for computer archiving and analysis of images. From the exposed variants of PP non-wovens taken from the sample on the frame, preparations were made and fixed to the base of the sample using self-adhesive carbon discs with a diameter of 10 mm. The surface of each preparation was coated with a conductive substance – gold. The surface of the samples was assessed by comparison of microscopic images of the sample exposed to light with microscopic images of the non-exposed sample at a magnification of 50 x and 3000 x [24]. The level of degradation was determined based on statistical analysis of the results of those measurements.

Table 1 below presents the intervals of exposure time and doses of solar and UV radiation for modified PP non-wovens.

The methodology of exposing the variants of non-wovens tested to xenon lamp light was consistent with the methodology of exposing the samples to sunlight, i.e. the same number of samples with the same dimensions was prepared. Samples were prepared in the form of three strips of PP non-woven with a width of 15 mm and length of 150 cm for a given variant of iron stearate concentration. The samples were fixed to standard clamps so that they were parallel to each other and did not overlap. The surface area of exposure was (121 x 35 mm). Before being placed in the Xenotest apparatus, each individual sample was weighed. After each series of exposure to xenon lamp light, the strength and mass of samples were measured, and they were assessed visually and in terms of topography. **Table 2** below presents the conditions in which the light exposure of modified PP non-wovens in the Xenotest Alpha HE apparatus took place.

Samples of modified PP non-wovens were exposed to artificial light accord-

Table 3. Time of exposure to the light of the xenon lamp in dependence on the value of radiation energy as the criterion for ending the exposure.

Radiation energy (sum from subsequent series), kJ/m ²		Time of exposure to the light of the xenon lamp
I	2 569	11h 53min
I+II	8 939	41h 23min
I+III	15 253	70h 37min
I+IV	23 800	110h 11min
I+V	32 515	150h 31min
I+VI	41 309	191h 15 min
I+VII	49 578	229h 31 min
I+VIII	57 608	266h 42 min
Total:		~ 1072 h

Table 4. Comparison of mass results of modified nonwoven samples: A/100, B/100, C/100, D/100 after exposure to sunlight.

Sample/ Series	Non-woven A/100			Non-woven B/100		
	Sample mass, g					
	Before exp.	After exp.	Weight change	Before exp.	After exp.	Weight change
Series I 2569 kJ/m ²	0.370	0.375	+0.005	0.367	0.373	+0.006
	0.374	0.380	+0.006	0.373	0.379	+0.006
	0.362	0.369	+0.007	0.348	0.356	+0.008
Series II 8939 kJ/m ²	0.340	0.348	+0.008	0.363	0.370	+0.007
	0.384	0.393	+0.009	0.374	0.381	+0.007
	0.392	0.400	+0.008	0.334	0.341	+0.007
Series III 15253kJ/m ²	0.305	0.310	+0.005	0.379	0.384	+0.005
	0.362	0.368	+0.006	0.321	0.326	+0.005
	0.348	0.354	+0.006	0.356	0.361	+0.005
Series IV 23800kJ/m ²	0.362	0.359	-0.003	0.357	0.344	-0.013
	0.362	0.361	-0.001	0.381	0.366	-0.015
	0.355	0.357	+0.002	0.374	0.368	-0.006
Series V 32515kJ/m ²	0.360	0.343	-0.017	0.343	0.318	-0.025
	0.392	0.385	-0.007	0.327	0.301	-0.026
	0.375	0.368	-0.007	0.341	0.317	-0.024
Sample/ Series	Non-woven C/100			Non-woven D/100		
	Sample mass, g					
	before exp.	after exp.	change weight	before exp.	after exp.	change weight
Series I 2569 kJ/m ²	0.333	0.342	+0.009	0.322	0.326	+0.004
	0.344	0.353	+0.009	0.312	0.14	+0.002
	0.331	0.342	+0.011	0.343	0.347	+0.004
Series II 8939 kJ/m ²	0.327	0.336	+0.009	0.360	0.368	+0.008
	0.309	0.318	+0.09	0.371	0.378	+0.007
	0.315	0.327	+0.012	0.349	0.357	+0.008
Series III 15253kJ/m ²	0.329	0.325	-0.004	0.294	0.277	-0.017
	0.343	0.340	-0.003	0.335	0.324	-0.011
	0.356	0.354	-0.002	0.330	0.316	-0.014
Series IV 23800kJ/m ²	only one sample was left very badly damaged			no samples for testing on the frame, tests ended		
Series V 32515kJ/m ²	no samples for testing on the frame, tests ended					

ing to the UV irradiance obtained in the corresponding series of exposure to sunlight. Subsequently, their tensile strength was tested as soon as possible after they were removed from the Xenotest apparatus. Such a procedure prevented further degradation of the fibres following removal from the apparatus. **Table 3** summarises the energies of UV radiation in individual series of exposure performed

under natural conditions and the time of exposure in the Xenotest.

Results and discussion

Assessment of changes in sample mass after exposure to sunlight and the xenon lamp light

Tables 4 and **5** present the variations in sample mass in relation to the time

Table 5. Comparison of mass results of modified nonwoven samples: A/100, B/100, C/100, D/100 after exposure in the Xenotest.

Sample/ Series	Non-woven A/100			Non-woven B/100		
	Sample mass, g			Sample mass, g		
	Before exp.	After exp.	Weight change	Before exp.	After exp.	Weight change
Series I 2569 kJ/m ²	0.292	0.291	-0.001	0.376	0.376	0.000
	0.326	0.327	+0.001	0.369	0.370	+0.001
	0.340	0.338	-0.002	0.375	0.373	-0.002
Series II 8939 kJ/m ²	0.304	0.303	-0.001	0.357	0.358	+0.001
	0.328	0.328	0.000	0.353	0.355	+0.002
	0.347	0.348	+0.001	0.363	0.364	+0.001
Series III 15253 kJ/m ²	0.339	0.339	0.000	0.378	0.378	0.000
	0.363	0.362	-0.001	0.320	0.321	+0.001
	0.358	0.356	-0.002	0.354	0.356	+0.002
Series IV 23800 kJ/m ²	0.340	0.341	+0.001	0.362	0.361	-0.001
	0.382	0.380	-0.002	0.374	0.374	0.000
	0.374	0.373	-0.001	0.330	0.329	-0.001
Series V 32515 kJ/m ²	0.376	0.375	-0.001	0.373	0.371	-0.002
	0.362	0.360	-0.002	0.370	0.369	-0.001
	0.378	0.377	-0.001	0.356	0.357	+0.001
Sample/ Series	Non-woven C/100			Non-woven D/100		
	Sample mass, g			Sample mass, g		
	Before exp.	After exp.	Change weight	Before exp.	After exp.	Change weight
Series I 2569 kJ/m ²	0.321	0.319	-0.002	0.328	0.328	0.000
	0.334	0.333	-0.001	0.339	0.340	+0.001
	0.348	0.349	+0.001	0.321	0.321	0.000
Series II 8939 kJ/m ²	0.343	0.343	0.000	0.327	0.328	+0.001
	0.333	0.334	+0.001	0.368	0.368	0.000
	0.331	0.330	-0.001	0.295	0.296	+0.001
Series III 15253 kJ/m ²	0.343	0.341	-0.002	0.329	0.327	-0.002
	0.350	0.349	-0.001	0.291	0.290	-0.001
	0.371	0.369	-0.002	0.326	0.323	-0.003
Series IV 23800 kJ/m ²	0.329	0.327	-0.002	0.318	0.316	-0.002
	0.337	0.336	-0.001	0.361	0.360	-0.001
	0.319	0.317	-0.002	0.336	0.334	-0.002
Series V 32515 kJ/m ²	0.350	0.348	-0.002	0.361	0.358	-0.003
	0.350	0.348	-0.002	0.343	0.342	-0.001
	0.331	0.330	-0.001	0.345	0.343	-0.002

of exposure to natural and xenon lamp light.

The average mass of sample strips from modified PP non-wovens, regardless of the assumed variant of the photodegradation activator, was 0.358 g. The average mass was calculated for all elementary samples prepared for light exposure. Due to the variability observed in the average mass values of the samples exposed to light – at a level of about 7% – the decision was made to analyse the masses of individual samples. In the case of the exposure of samples to natural light, the growths in sample mass calculated at the initial stage of exposure amounted to approx. (2.5 to 3.0%) in relation to the initial mass of samples. This was most likely due to the settling of pollutants on the surface of the samples or to rainfall. During the next series of exposure to light,

the percentage value of loss increased to max (10-11%) of the initial sample mass. The largest mass loss was recorded for the D/100 variant.

In the case of the exposure of samples to xenon lamp light, the mass loss was at a very low level of approx (0.4 to 0.7%). The cases observed of an increase in the mass of samples exposed to light in the Xenotest apparatus – at a maximum level of 0.6% – might have been caused by the fact that the test was completed immediately after an irrigation cycle. It was assumed in the experiment that the tests were performed immediately after completion of the processes of exposure to light in order to prevent further uncontrolled degradation of the samples.

When analysing the changes in the mass of modified PP non-woven samples ex-

posed to natural light and xenon lamp light during the experiment, one can conclude that the processes of natural exposure to light carried out on the sample exposure stand affect the change in the mass of non-wovens, and these are visible elements of the photodegradation process. The process of photodegradation of non-wovens caused by xenon lamp light did not cause significant changes in the sample mass.

Tensile strength after exposure to sunlight and xenon lamp light

Tables 6-7 summarise the results of tensile strength tests of modified PP non-wovens exposed to natural and xenon lamp light after successive series of exposure. Statistical values are given for three working samples tested; in the remaining cases, the average value or the value of a single measurement is given.

The analysis of breaking strength values for the modified PP non-wovens allows to conclude that A/100 retains the strength properties for the longest period both when exposed to sunlight and xenon lamp light.

The strength values for the A/100 sample in the 1st and 2nd series of exposure reached 90.5% and 79% of the breaking strength value. After the 3rd series of exposure, the A/100 test variant retained 50% of the breaking strength value. After the 5th series of exposure to natural light, the breaking strength value reached 8.3%. After the 6th series of testing, one sample out of three remained, reaching 0.7 N, which is only 2.3% of the breaking strength value for the samples before exposure. After the 5th series of exposure, the value is 45%, and after the 6th series it reaches ¼ of the value for the sample before exposure.

For the B/100 variant, the tests were terminated after the 5th series because the values obtained after the 6th series were close to zero. Like for the A/100 sample, the breaking strength reached 89% after the 1st series and 71% after the 2nd series, respectively. The breaking strength value after the 3rd series decreased to 34%. After the 4th series of exposure to sunlight, the B/100 variant retained 38% of the breaking strength value, and after the 5th series the value decreased significantly, reaching 8.8% of the pre-exposure value. For the C/100 and D/100 samples, the tests were completed after the 3rd se-

Table 6. Results of tensile strength tests of modified PP non-wovens: A/100. B/100. C/100. D/100 exposed to natural and xenon lamp light.

Sample/Series/ Radiation energy	Non-woven A/100		Non-woven B/100		Non-woven C/100		Non-woven D/100	
	Strength max, N							
	Natural light	Xenon lamp	Natural light	Xenon lamp	Natural light	Xenon lamp	Natural light	Xenon lamp
Before exposure	29.8	29.8	28.3	28.3	31.3	31.3	33.8	33.8
	29.9	29.9	25.7	25.7	30.8	30.8	33.8	33.8
	31.9	31.9	27.5	27.5	28.4	28.4	31.9	31.9
\bar{X}	30.5	30.5	27.2	27.2	30.2	30.2	33.1	33.1
s	1.18	1.18	1.31	1.31	1.55	1.55	1.07	1.07
CV	3.9	3.9	4.8	4.8	5.1	5.1	3.2	3.2
Series I 2 569 kJ/m ²	30.1	25.4	22.1	29.9	14.8	29.5	9.4	28.1
	26.0	22.0	25.4	30.7	13.1	29.0	11.4	27.1
	26.7	23.2	25.0	27.9	12.5	28.8	8.6	28.8
\bar{X}	27.6	23.5	24.2	29.5	13.5	29.1	9.8	28.0
s	2.22	1.71	1.81	1.44	1.17	0.37	1.45	0.89
CV	8.0	7.3	7.5	4.9	8.7	1.3	14.8	3.2
Series II 8 939 kJ/m ²	17.2	31.9	24.7	19.4	3.7	3.1	2.4	2.3
	30.8	21.7	20.0	22.6	2.1	4.3	2.6	5.6
	24.7	24.9	13.3	22.5	2.2	5.2	2.1	5.1
\bar{X}	24.2	26.2	19.3	21.5	2.7	4.2	2.4	4.3
s	6.82	5.24	5.74	1.83	0.86	1.03	0.27	1.80
CV	28.2	20.0	29.7	8.5	32.2	24.6	11.0	41.5
Series III 15 253 kJ/m ²	9.0	13.3	6.7	25.3	0.6	6.9	0.2	16.4
	21.7	17.4	9.6	22.7	0.8	11.1	0.2	15.9
	15.7	14.8	11.7	21.6	1.2	13.0	0.2	18.4
\bar{X}	15.5	15.2	9.3	23.2	0.9	10.3	0.2	16.9
s	6.36	2.09	2.52	1.89	0.29	3.12	0.02	1.31
CV	41.2	13.8	27.1	8.2	33.4	30.3	9.5	7.8
Series IV 23 800 kJ/m ²	8.3	15.4	5.3	10.9	–	0.9	–	–
	9.9	19.3	2.8	9.7	–	–	–	–
	9.2	16.3	4.9	10.3	–	–	–	–
\bar{X}	9.1	17.0	4.3	10.3	–	0.9	–	–
s	0.79	2.08	1.36	0.61	–	0	–	–
CV	8.7	12.2	31.4	5.9	–	0	–	–
Series V 32 515 kJ/m ²	2.2	8.3	1.3	1.9	–	–	–	–
	2.8	4.7	1.2	1.7	–	–	–	–
	2.8	6.2	1.3	3.5	–	–	–	–
\bar{X}	2.6	6.4	1.3	2.4	–	–	–	–
s	0.34	1.84	0.05	1.00	–	–	–	–
CV	13.2	28.7	4.0	42.1	–	–	–	–
Series VI 41 3095 kJ/m ²	0.9	2.5	–	0.3	–	–	–	–
	1.0	2.6	–	–	–	–	–	–
	–	–	–	–	–	–	–	–
\bar{X}	0.9	2.5	–	0.3	–	–	–	–
s	–	–	–	–	–	–	–	–
CV	–	–	–	–	–	–	–	–

tensile tests completed

ries, where the breaking strength values reached a level of less than 1 N.

In the case of exposure to xenon lamp light, strength properties were maintained at a level of 50-60% up to the 4th series (breaking strength) of light exposure for samples A/100 and B/100. In the 2nd series, the breaking strength values for the variants presented were 86% and 79%. In the 5th series of exposure, there was a significant decrease in strength, reaching 21% of the initial value for the A/100 sample and 8.8% for the B/100 variant. In

the case of modified PP non-woven variants C/100 and D/100, the results obtained indicate that a good level of the breaking strength value was retained after exposure to sunlight only until the first series of exposure – 45% and 30%, respectively. After the 3rd series of light exposure, breaking strength values for the C/100 and D/100 variants were at a level of 14% and 13% in relation to the initial strength.

It is worth commenting here on the relative elongation values calculated for the PP non-wovens. They may be explained

by observation of the course of the tensile strength tests and the structure of the test samples itself. After the last phase of exposing non-wovens to light, a significant change in structure was observed organoleptically during the strength tests. With a constant 100 mm/min increase in the force of displacement of the machine clamps, fibres of the non-woven tested were observed to move apart at a still slightly increasing force.

Table 7 presents the results of tensile strength tests of non-modified PP non-

Table 7. Results of tensile strength tests of non-modified PP non-woven variant 0/100 and modified PP non-woven variants A/100 and B/100 exposed to sunlight.

Sample/Series/ Radiation energy	Non-woven 0/100		Non-woven A/100		Non-woven B/100	
	Strength max, N	Elongation at max force, %	Strength max, N	Elongation at max force, %	Strength max, N	Elongation at max force, %
Before exposure	21.4	10.2	29.8	10.7	28.3	8.7
	21.4	10.5	29.9	9.7	25.7	8.5
	20.0	9.8	31.9	9.5	27.5	8.7
\bar{X}	20.9	10.2	30.5	9.9	27.2	8.6
s	0.8	0.3	1.18	0.63	1.31	0.10
CV	3.9	3.3	3.9	6.3	4.8	1.1
Series I 6 235 kJ/m ²	20.3	11.7	25.5	9.7	29.1	10.5
	20.0	11.5	27.6	10.0	28.8	10.3
	20.3	10.8	22.5	8.5	24.9	9.5
\bar{X}	20.2	11.3	25.2	9.4	27.6	10.1
s	0.2	0.4	2.5	0.8	2.3	0.54
CV	0.9	3.9	10	8.4	8.4	5.30
Series II 14 410 kJ/m ²	18.9	9.2	24.1	8.7	19.0	6.8
	13.2	7.2	24.2	8.5	18.3	6.2
	14.0	8.5	25.9	9.2	17.8	5.7
\bar{X}	15.4	8.3	25.7	8.8	18.4	6.2
s	3.1	1.0	1.0	0.4	0.6	0.6
CV	20	12	4.0	3.9	3.1	9.4
Series III 23 900 kJ/m ²	19.4	10.0	17.3	8.7	11.1	7.0
	14.6	9.7	16.7	7.8	10.9	7.2
	13.4	9.5	16.5	8.7	10.0	6.6
\bar{X}	15.8	10.0	16.8	8.4	10.6	6.9
s	3.2	0.7	0.5	0.5	0.6	0.4
CV	20	7.3	2.6	5.7	5.3	5.0

tensile tests completed

woven variant 0/100 and modified PP non-woven variants A/100 and B/100 exposed to sunlight.

Tests under natural conditions for the A/100 variant with an activator concentration of 0.02% were terminated after the 6th series, and for the B/100 variant with an activator concentration of 0.05% – after the 5th series of light exposure. The tests entailing exposure to xenon lamp light were terminated for the A/100 variant of the activator after the 7th series, and for the B/100 variant after the 6th series of light exposure, respectively. It was observed that PP non-woven samples exposed outdoors degraded more intensively than those tested in the Xenotest. That observation is confirmed by the maximum force for elongation tests. Despite the fact that the intensity of the UV xenon lamp light was equal to solar UV radiation in each batch of irradiation, the Xenotest apparatus could not fully simulate outdoor weather conditions. In addition, the degradation process proceeded faster in sunlight due to weather conditions such as wind and rain, which strained the structure of the nonwovens.

Analysis of the decrease in the strength of the 0/100 non-woven without the ad-

dition of a photodegradation activator confirmed that the rate of change in the tensile strength of this sample is slower than for the modified samples. The 0/100 sample after the 3rd series of light exposure retained approximately 70% of the maximum tensile strength value as compared to the A/100 variant sample, which retained approx. 55% of the maximum tensile strength value after the 3rd series. The results obtained indicate that the tensile strength of the non-wovens analyzed depends on the concentration of the activator in the fibre mass and on the method of exposure. The smaller the percentage of the activator, the greater the strength of the non-woven per unit of time.

Changes in the relative elongation value at the breaking strength for four test samples indicate the variability in the value of this parameter during the light exposure processes. The elongation values locally decrease and increase, and after completing the exposure of non-woven samples to light, they reach a level that is significantly lower in each case than the initial elongation values. These phenomena, both as regards the values of forces and elongations, may be caused by the structural variability that is typical of non-wovens, as indicated by the calcu-

lated values of the force and elongation variability coefficient – characterised by a spread of 1-30%.

Figure 1 presents the tensile breaking strength and relative elongation values for modified PP non-wovens in subsequent series of exposure to sunlight and xenon lamp light, and the relative change in the value of the tensile breaking strength and relative elongation at the breaking strength in relation to the pre-exposure values.

Observation of the diagrams in **Figure 1** shows that these changes, regardless of the non-woven variant and its mass per unit area, are more intense in the case of exposure to sunlight. The force values decrease following successive series of light exposure. The fastest photodegradation, as determined by the change in tensile strength, occurs for the D/100 variant of non-woven, followed by C/100. In this case, it was possible to perform strength testing up to the 3rd series of exposure under natural conditions. Further exposure of samples to light led to severe structural damage, which prevented tests on the strength testing machine. For the A/100 and B/100 variants of non-woven, local increases in the breaking strength

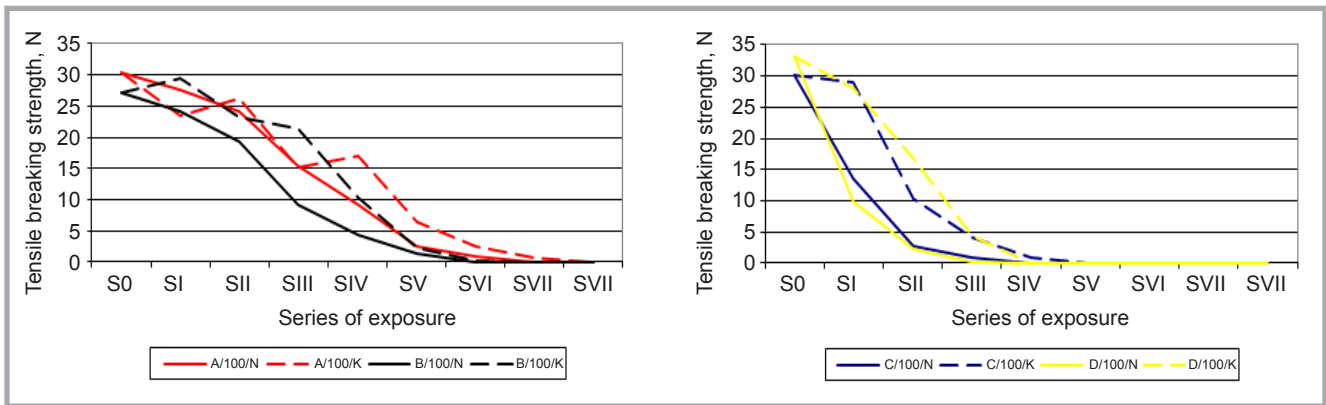


Figure 1. Changes in the tensile breaking strength value for modified PP non-wovens in subsequent series of exposure to sunlight and xenon lamp light. Continuous lines indicate changes in the breaking strength and elongation values for variants of non-wovens exposed to sunlight, and dashed lines show changes in the breaking strength and relative elongation values for the variants of PP non-wovens exposed to xenon lamp light.

value can be observed. They were calculated for samples of PP non-wovens exposed to xenon lamp light.

Visual assessment of the appearance of samples of modified PP non-wovens following the process of exposure to natural and xenon lamp light was performed by the organoleptic assessment of changes in the appearance of samples immediately after exposure. **Figure 2** presents selected photographs of samples exposed to sunlight – marked N; and xenon lamp light – marked Xe. Photographs were taken after the 4th series of exposure at a recorded irradiance of 23 000 kJ/m².

Observation of the diagrams in **Figure 2** shows that these changes, regardless of the non-woven variant and its mass per unit area, are more intense in the case of exposure to sunlight. The force values decrease following successive series of light exposure. The fastest photodegradation, as determined by the change in tensile strength, occurs for the D/100 variant of non-woven, followed by C/100. In this case, it was possible to perform strength testing up to the 3rd series of exposure under natural conditions. Further exposure of samples to light led to severe structural damage, which prevented tests on the strength testing machine. For the A/100 and B/100 variants of non-woven, local increases in the breaking strength value can be observed. They were calculated for samples of PP non-wovens exposed to xenon lamp light.

Visual assessment of the appearance of samples of modified PP non-wovens following the process of exposure to natural and xenon lamp light was performed by the organoleptic assessment of changes

in the appearance of samples immediately after exposure. **Figure 2** presents selected photographs of samples exposed to sunlight – marked N, and xenon lamp light – marked Xe. They were taken after the 4th series of exposure at a recorded irradiance of 23 000 kJ/m².

The photographs of non-woven samples demonstrate the most representative changes in the appearance of non-wo-

vens observed during sunlight exposure tests. These changes feature the destruction of PP non-wovens on a microscopic scale. The structure of the A/100 variant of non-woven is best preserved. In the case of the D/100 variant of non-woven, its virtually total photodegradation occurred after the 4th series of light exposure. The thinning and defects in the structure of the non-woven and the deformation of the sample dimensions can be

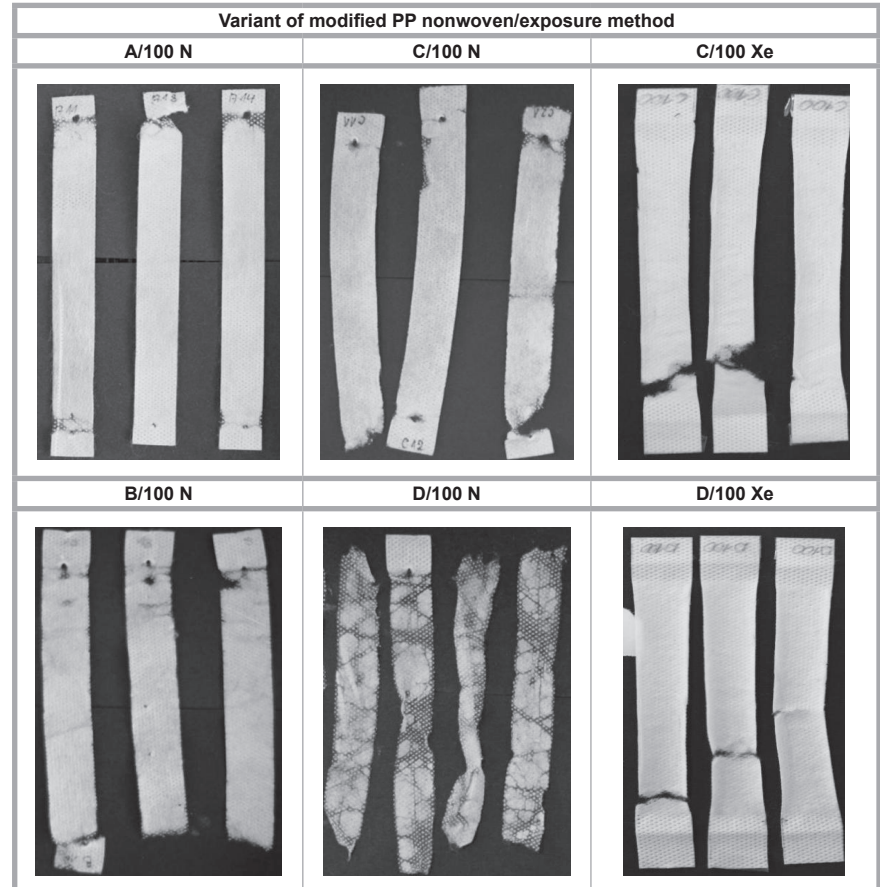


Figure 2. The appearance of samples of modified PP nonwovens after IV series of sunlight exposure and xenon lamp light. Radiation intensity 23 800 kJ/m².

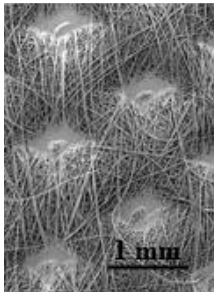
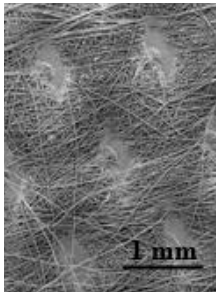
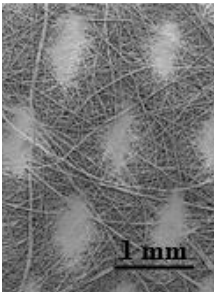

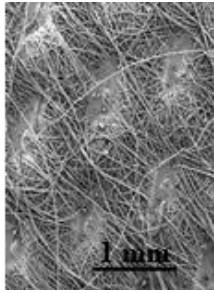
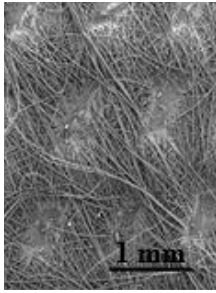
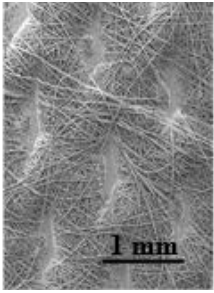

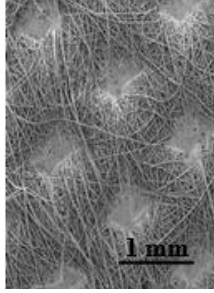
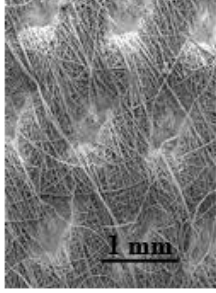
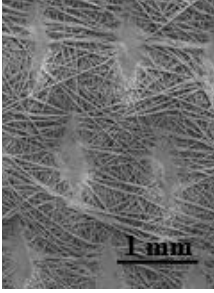
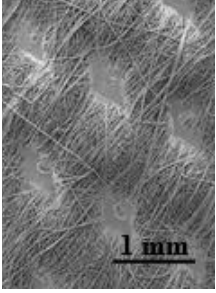
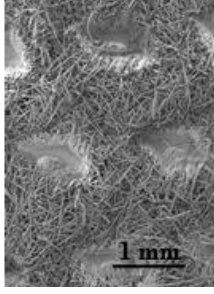
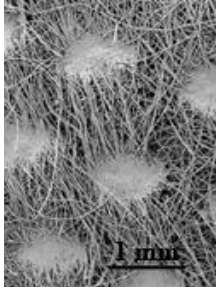
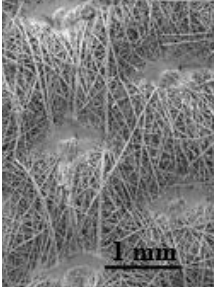
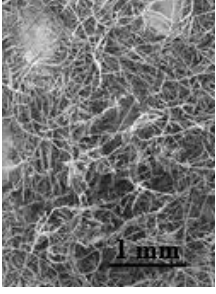
Exposure series/ Radiation energy	Non-woven A/100	Non-woven B/100	Non-woven C/100	Non-woven D/100
Before exposure				
I series I/ 2 569 kJ/m ²				
II series I + II/ 8 939 kJ/m ²				
IV series I + IV/ 23 800 kJ/m ²				

Figure 3. Summary of selected microscopic images of the structure of samples of modified PP nonwovens with a surface mass of 100 g/m² irradiated with sunlight at a magnification of 50x.

clearly seen. It was difficult to perform tensile strength tests of such samples, and in the case of the D/100 sample, it was no longer possible due to the fact that the samples were further broken down as a result of touch and attempts to attach them to the clamps of the strength testing machine.

Structural topography of non-wovens exposed to sunlight

Figures 3-4 present selected microscopic images of modified PP non-woven samples exposed to sunlight. Microscopic

images of non-wovens were taken at a magnification of 50 times, whereas those of non-woven fibres were taken at a magnification of 3 000 times. The photographs were selected to demonstrate the most characteristic structural changes in the samples, which could be observed for a given variant of non-woven at a certain stage of exposure to sunlight.

Based on the analysis of the microscopic images obtained, it can be observed that after the 1st series of light exposure (2 569 kJ/m²), changes were observed in

the form of fractures and damage to single fibres for the C/100 and D/100 non-wovens. No changes in surface topography were observed for other samples of modified PP non-wovens. After the second series of exposure to sunlight (8 939 kJ/m²) of non-woven variants B/100, C/100 and D/100, the number of fractures observed increased with the concentration of the photodegradation activator. No visible changes affecting the fibres were observed for the A/100 non-woven. After 6 weeks of exposure to light, i.e. for the 3rd series – 15 253 kJ/m²,

Exposure series/ Radiation energy	Non-woven A/100	Non-woven B/100	Non-woven C/100	Non-woven D/100
Series I + II/ 8 939 kJ/m ²				
Series I + III/ 15 253 kJ/m ²				
Series I + IV/ 23 800 kJ/m ²				—
Series I + V/ 32 515 kJ/m ²			—	—
Series I + VI/ 41 309 kJ/m ²			—	—
Series I + VII/ 49 578 kJ/m ²			—	—
Series I + VIII/ 57 608 kJ/m ²		—	—	—

Figure 4. Summary of selected microscopic images of samples of modified PP nonwovens with a surface mass of 100 g/m² irradiated with sunlight at a magnification of 3000x.

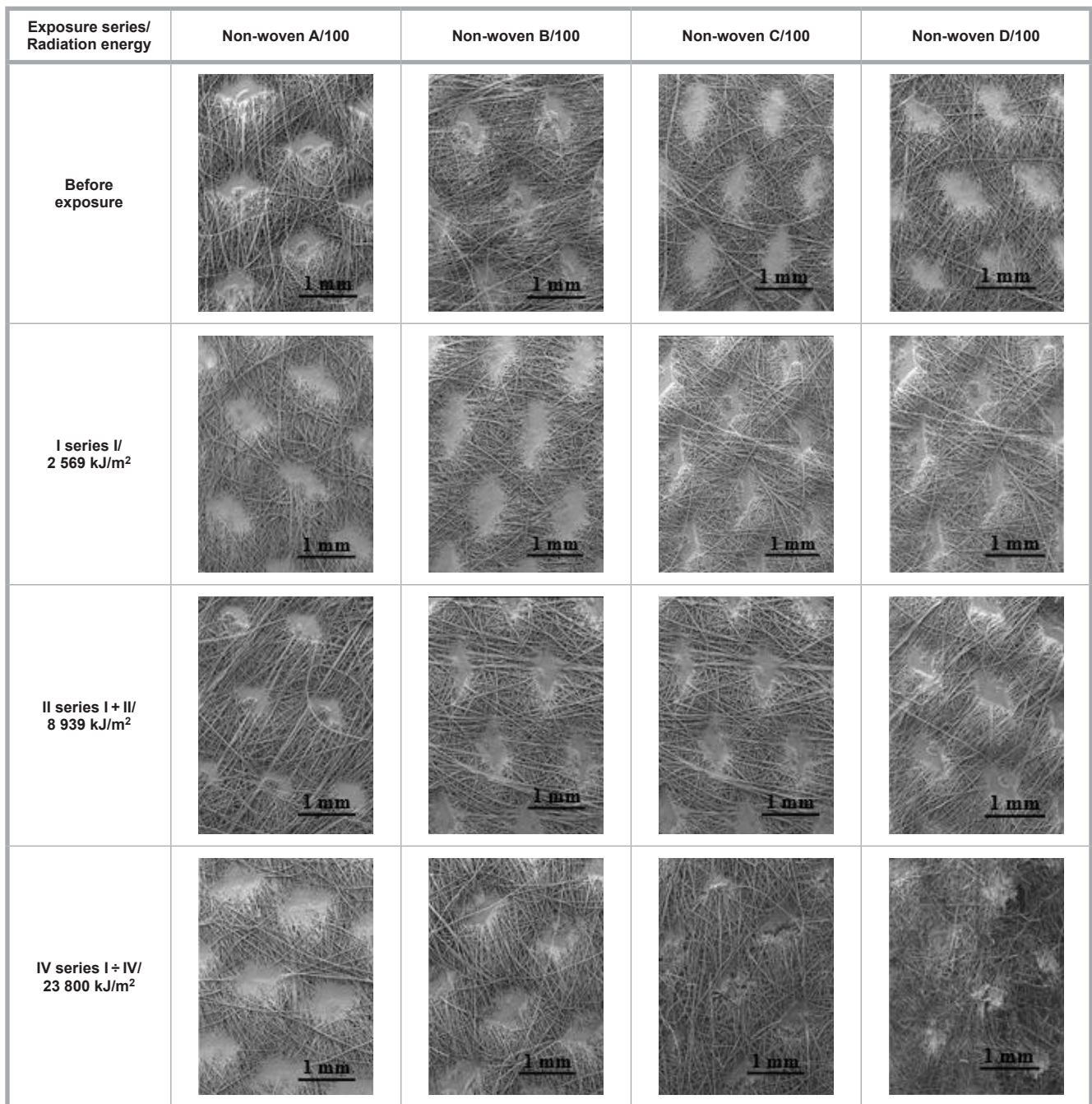


Figure 5. Summary of the microscopic images of modified non-wovens exposed to xenon lamp light at a magnification of 50x.

there were fractured fibres and clusters of fractured fibres in samples A/100, B/100 and C/100, whereas in the case of the D/100 sample, the structure of the non-woven was damaged. In samples A/100 and B/100, there were numerous transverse fractures of the fibre surface that are characteristic of the photodegradation process. After 8 weeks of exposure to light, i.e. for the 4th series – 23 800 kJ/m², the structure of samples marked B/100 and C/100 was damaged, and a large number of fractured fibres with characteristic transverse cracks occurred on the surface of the A/100 sample. The D/100 non-woven

sample disintegrated completely, and its exposure to light was discontinued.

After 10 weeks of exposure to light, i.e. for the 5th series – 32 515 kJ/m², there were clusters of fractured fibres in the A/100 sample, and the structure of the B/100 non-woven sample was damaged, whereas the remaining samples, C/100 and D/100, were completely destroyed, and their exposure to light was discontinued.

The first significant changes in the appearance of samples were noticed af-

ter 6 weeks of exposure to light. It was clearly visible that the non-woven structure had been deformed, and numerous fractured fibres were visible. For samples B/100, C/100 and D/100, defects in the structure of the non-woven were clearly visible after 10 weeks of exposure to light.

Structural topography of non-wovens exposed to xenon lamp light

Figure 5 summarises the microscopic images of modified non-wovens exposed to xenon lamp light at a magnification of 50x. Based on the analysis of the images

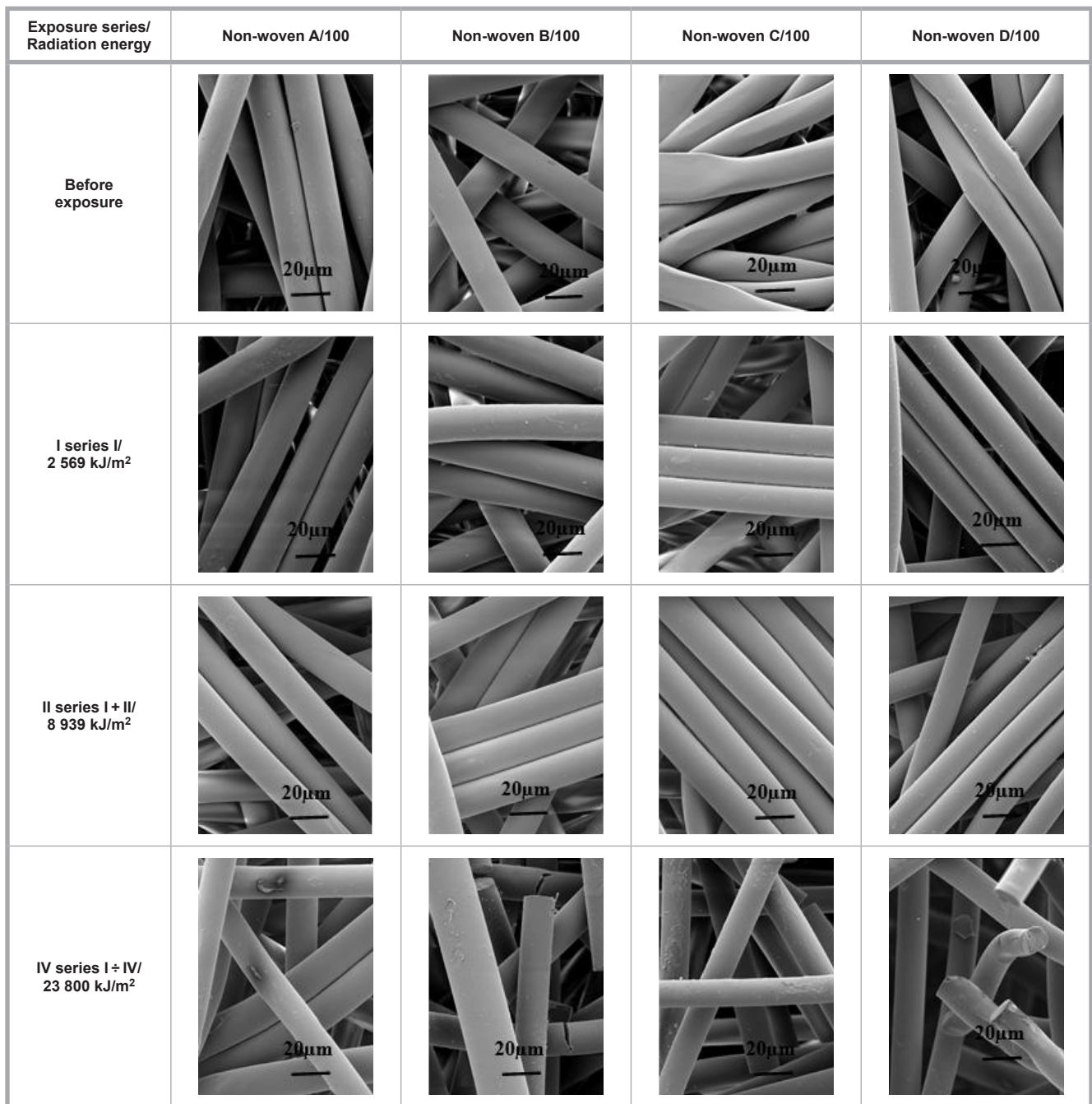


Figure 6. Summary of the microscopic images of modified non-wovens exposed to xenon lamp light at a magnification of 3000x.

obtained, the most visible changes in the structure of the non-woven after exposure to xenon lamp light were observed for the D/100 variant after the 4th series of exposure and for variants C/100 and D/100 after the 5th series.

A radiation dose of up to 8 939 kJ/m² does not cause visible changes on the surface of fibres. Larger doses of radiation already cause clear changes in the surface topography.

Under natural conditions, photodegradation of the D/100 non-woven was the

fastest. At a dose of solar radiation of 2 569 kJ/m², i.e. after the 1st series, single fractures of elementary fibres were observed, and at a dose of 8 939 kJ/m², i.e. after the 2nd series, the fibre surface was completely destroyed and transverse fractures of all fibres observed. Photodegradation of the C/100 non-woven upon exposure to light is somewhat slower. Single transverse fractures appeared after exposure to sunlight at a radiation dose of 8 939 kJ/m², and after exposure at a dose of 23 800 kJ/m² – 4th series, the fibre surface was densely intersected by deep and wide

transverse fractures. For the B/100 sample, individual fibre fractures were observed during the 3rd series at a dose of 15 253 kJ/m², and in the 4th series shallow, frequent and short fractures appeared on the fibre surface, which continued up to the 6th series at a dose of 49 578 kJ/m², where fibre fractures were observed for each individual fibre. The A/100 sample remained with few fractured/broken individual fibres up to the 8th series at a dose of 57 608 kJ/m². The surface of the elementary fibres had numerous, shallow and short fractures, which appeared in the microscopic im-

age starting from a dose of 15 253 kJ/m² during the 3rd series.

The process of photodegradation under xenon lamp light was much more moderate. After the 2nd series of exposure, the fibres of all four samples remained intact. Differences in the appearance of the fibre surface can be observed after the subsequent series of exposure to light, which occur in the form of totally broken fibres. It is significant that there were no small fractures on the fibre surface that typically occurred during the microscopic observation of the fibres exposed to natural light. The most visible changes in the structure of the non-wovens were observed for the D/100 variant after the 4th series of exposure to light and for the C/100 and D/100 variants after the 5th series of exposure to xenon lamp light.

Assessment of the appearance of the samples of modified PP non-wovens exposed to natural light and xenon lamp light makes it possible to confirm the microscopic observations that the test conditions on the Xenotest apparatus are not able to fully simulate outdoor conditions, and the course of structural changes, although identical in nature, proceeds slightly differently in both cases of exposure to light. The same macroscopic structural changes occur at different exposure times and depend on the exposure method. However, the method of exposure to artificial light, in this case using xenon lamp light, is the only tool, and a very good one, for simulating the photodegradation process under laboratory conditions, allowing the process to be evaluated in a relatively short time. Its advantage is that an objective test methodology is obtained, which is impossible in the case of proving ground tests due to the unpredictable variability in outdoor conditions.

Conclusions

A comparative analysis of changes in the mass per unit area, strength and structural topography of the samples exposed to sunlight and xenon lamp light showed that sunlight affects the photodegradation of modified PP non-wovens more strongly than xenon lamp light. Microscopic analysis showed that the photodegradation process of modified PP non-wovens strongly depends on the concentration of the activator in the fibre mass and on the method of exposure of modified non-wovens to light. The highest resistance to

exposure of the samples assessed on the basis of the tensile strength was recorded for non-wovens with photodegradation activator concentrations of A – 0.02% and B – 0.05%. Such changes were observed despite the fact that the energy of the UV radiation of the xenon lamp in each series of exposure corresponded to the UV radiation energy of sunlight. Analysis of the decrease in strength of the comparator (reference material), i.e. non-woven without the addition of a photodegradation activator, confirmed that the rate of change in tensile strength is slower than for modified samples. A comparative analysis of changes in the strength and topography of samples exposed to sunlight and xenon lamp light showed that sunlight affects the photodegradation of modified PP non-wovens more strongly than xenon lamp light, despite the same UV radiation energy used for tests. It was observed that PP non-woven samples exposed outdoors photodegraded more intensively than those tested in the Xenotest. This observation is confirmed by the maximum force obtained for elongation tests, as well as by SEM microscopic examination. Differences in the photodegradation rate of non-wovens under the influence of artificial light and sunlight may be due to the variation in the day/night cycle during exposure under natural conditions as well as the difference in the temperature of the exposed samples or that in their humidity. This allows to conclude that the test conditions in the Xenotest are not fully able to simulate outdoor conditions. The maximum force at failure and microscopic analysis of the progress of the photodegradation process of the modified PP non-wovens and the rationale for the selection of a given activator concentration in the fibre mass. Analysis of the decrease in the strength of the reference material (comparator), i.e. the non-woven without the addition of a photodegradation activator, confirmed that the rate of change in the tensile strength of that sample is slower than for modified samples. The sample after the 3rd series of light exposure retained approximately 70% of the maximum tensile strength value as compared to the A – 0.02% variant sample, which retained approx. 55% of the maximum tensile strength value after the 3rd series. It is worth noting that the maximum force at elongation and SEM microscopic analysis are only tools for the assessment of the photodegradation process of modified PP non-wovens and of the rationale for

the selection of a given modifying agent concentration in the fibre mass.

Non-wovens were tested for photodegradation under real field conditions in order to assess their potential applicability in agriculture in [21].

Acknowledgements

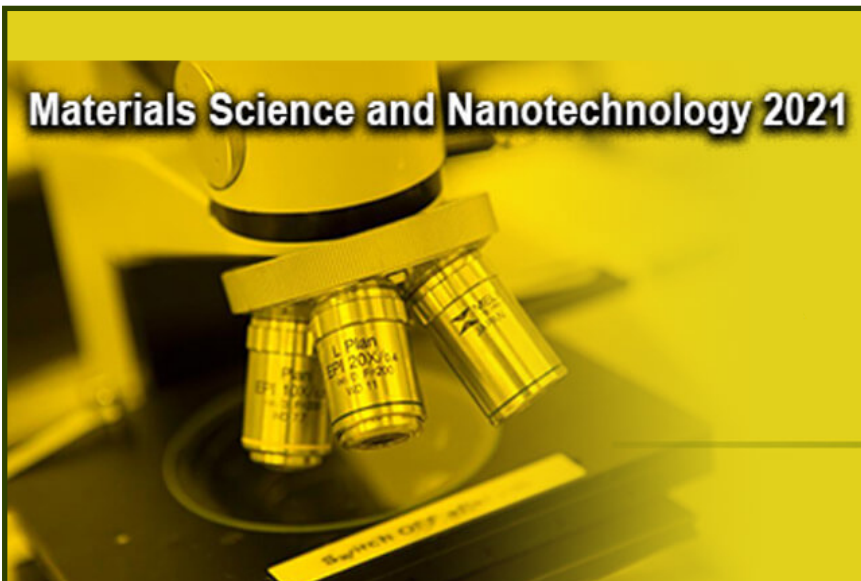
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