

Influence of Modification on the Structural and Tensile Properties of Polyurethane Coated Knitted Fabrics after Natural Weathering

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Abstract

The intention of this study was to investigate the changes in properties of polyurethane coated knitted fabrics intended for sportswear or casual wear, i.e. outdoor use after natural weathering, in two different seasons. The exposure of coated fabrics to outdoor natural weathering affected all properties investigated, namely, the mass, thickness, shrinkage, elongation and breaking forces. Summer exposure made greater modification of every parameter measured than winter exposure, except for the thickness. Solar radiation has a greater impact on the decrease in breaking forces of coated fabrics than on other properties measured. Strong positive correlations between the thickness of coated fabric and breaking forces were observed which can be used to design coated fabric with better tensile properties. The prediction of change under the influence of environmental conditions allows to improve coated fabrics with the aim of better protection of the wearer.

Key words: natural weathering, coated knitted fabrics, structural properties, tensile properties.

■ Introduction

Polyurethane-coated knitted fabrics have certain suitability for outdoor casual wear which is worth studying. They are generally more stretchable and elastic than coated fabrics with a woven substrate. A knitted substrate can be designed to meet different structural and tensile requirements by varying the type of knit, density, thickness, mass and yarn count. Polyurethane coatings in comparison to other polymers have greater resistance to abrasion and splitting, as well as increased strength and durability. The treatment of polyurethane-coated knitted fabrics can be antibacterial, antiallergic, fungus and mildew treated, antistatic and flame-retardant [1, 2].

Due to the fact that such garments are often exposed to specific weather conditions, information about the change in tensile properties after exposure is very valuable. The weatherability of coated textiles has been mostly researched at high loads of coated fabric used in the building industry. Cracking and peeling of the coating were more evident on PVC-coated as compared to PTFE-coated fabrics. The effect of different thicknesses of coating on the stability of materials was observed in [3]. Also the importance of thickness for maintaining mechanical properties was noticed by Eichert [4]. The natural weathering conducted showed that besides the UV exposure,

air pollution has the biggest influence on the degradation of coated industrial fabric [5]. Research conducted by Defflorian showed that the accelerated UV exposure test is not sufficient to simulate natural exposure. The coating thickness has a strong influence on accelerated weathering results [6]. In another study [7], the regression models that should be used to predict the thermal behaviour of weathered polyurethane coated fabrics are given. Boubakry et al observed the impact of ageing on the mechanical properties of thermoplastic polyurethanes. The degradation of mechanical properties seemed to be well correlated to observations obtained from SEM photographs [8].

Tests of the elongation properties of coated knitted fabrics are rare. Coated woven fabrics have been more frequently tested. The influence of polyurethane coatings and woven fabric structure on the properties of composites [9], tensile strength [10], anisotropy [11] and the adhesion between layers [12] was tested. Among coated knitted fabrics, multi-axial coated warp-knitted fabrics were mostly tested because they find wide technical application [13, 14]. The elongation properties of coated knitted fabrics suitable for making protective, work and sports clothing were tested in other papers [2, 15], but according to the authors' knowledge, coated knitted fabrics intended for outdoor sportswear were not exposed to weathering in different seasons.

■ Experimental

Samples and structural properties

Seven knitted fabrics with different structures were selected for the substrates of coated fabrics with the aim of covering a wide interval of values of the characteristics tested. The mass per unit area of the fabrics chosen is from 47 g/m² to 184 g/m², and the breaking force of the substrate during spherical breakage is from 73.33 N to 1058.3 N. Constructional parameters of the fabric tested (designated CF1-CF7) are in **Table 1**, and tensile parameters of the test fabric in **Table 2**.

They were coated under the same conditions on the same coating line of the Recomo Company, Germany [16]. Polyurethane was applied to knitted fabric using the transfer procedure. Polyurethane paste was also applied to the backing paper using a pump. The coatings were adjusted in the distance between the knife on which the polyurethane paste was applied and the roller under the knife. The polyurethane coatings have nearly equal average thickness (0.16 mm) and

weight (80 g/m²). The polyurethane paste applied with the paper passed through a dryer, where the temperature was adjusted to 80 °C. Another coating of the same polyurethane paste was applied in the same way. The final coating was a polyurethane binding agent on which the knitted fabric was laminated. The binder was cross linked in the dryer at 160 °C.

Measuring method

Ageing of the coated fabric was carried out in conformity with Standard EN ISO 877-1:2010 – Methods of exposure to solar radiation – Part 1: General guidance and with EN ISO 877-2:2010 – Part 2: Direct weathering [17, 18].

Fabrics are placed on a rack that is made of untreated wood, inert material that does not affect the test results. Exposures at tilt angles of 5° or 45° to the horizontal are very commonly used for plastics. Since the location of exposure is lat.: 45° N, long.: 16° E the exposure angle is fixed at 45° facing the equator, which not only simplifies comparison with established results but ensures good total solar

radiation since the tilt angle is the same as the latitude.

The number and dimensions of the test specimens were those specified in the appropriate test method for determination of the tensile strength and elongation at break. Specimens were exposed in an unstrained state in such a manner that there is a free flow of air against the front and back of the specimen – so-called open exposure. Regular inspection of the site for the purpose of refixing loose test specimens, particularly after storms, was performed.

Samples of coated textiles were exposed to summer and winter weather conditions.

The duration of exposure of samples during the summer season was from 15th of July to 15th of October, and during the winter season from 1st of December to 1st of March.

Climatic conditions during the test were monitored and reported by courtesy of the Croatian meteorological and hy-

Table 1. Constructional parameters of knitted substrate of coated fabric.

Sample of coated fabric	Structure of substrate	Yarn count, dtex	Material composition of substrate	Mass per unit area of substrate, g/m ²	Thickness of substrate, mm	Density per cm wales/courses
CF1	Simplex	55	PA	184	0.74	18/17
CF2	Locknit	111	PA	152	0.62	14/24
CF3	Power-net	17	PES	47	0.26	10/60
CF4	Voile	17	PES	60	0.32	12/54
CF5	Power-net	13	PA	134	0.40	12/68
CF6	Plain structure	156	PA	110	0.68	11/16
CF7	Interlock	133	PES	109	0.50	15/15

Table 2. Tensile parameters of knitted substrate of coated fabric.

Sample of coated fabric	Elongation of substrate, wale direction, %	Elongation of substrate, course direction, %	Breaking force of substrate, wale direction, N	Breaking force of substrate, course direction, N	Breaking force of substrate, spherical breakage, N
CF1	116.35	126.49	907.52	501.82	1058.3
CF2	107.2	102.88	347.64	429.3	651.7
CF3	46.41	34.96	117.99	66.27	102.5
CF4	124.97	49.11	104.61	71.71	73.33
CF5	309.93	145.22	237.48	185.68	113.33
CF6	101.15	157.93	264.29	212.09	351.67
CF7	65.91	151.21	384.03	212.12	581.7

Table 3. Climatic conditions during the test.

Duration of exposure	Total solar radiant exposure, J/cm ²	Temperature – t – monthly mean of daily mean, °C	Relative humidity – Rh – monthly mean of daily mean, %	Precipitation – R – monthly total of rainfall, mm	Precipitation – S – monthly total of snow, cm
15.7.–15.10. summer season	47878	19.1	66	147.4	0
1.12.–1.3. winter season	24046	1.4	75	130.2	29

Table 4. Properties of coated fabric before and after weathering.

Sample of coated fabric	Total mass per unit area, g/m ²			Thickness, mm			Shrinkage, %		
	Before	Summer s.	Winter s.	Before	Summer s.	Winter s.	Before	Summer s.	Winter s.
CF1	283	284	290	0.78	0.78	0.78	/	6.5	2.8
CF2	249	248	257	0.62	0.59	0.59	/	5.5	2.6
CF3	130	125	141	0.3	0.27	0.27	/	6.5	2.1
CF4	147	141	147	0.4	0.38	0.38	/	3.2	1.6
CF5	238	234	248	0.47	0.46	0.46	/	3.1	2.0
CF6	174	186	181	0.61	0.6	0.61	/	4.2	2.0
CF7	196	192	190	0.52	0.51	0.52	/	1.3	1.0

Table 5. Elongation properties of coated fabric before and after weathering.

Sample of coated knitted f.	Average elongation in the wale direction – ϵ_{cw} , %			Average elongation in the course direction – ϵ_{cc} , %		
	Before	Summer s.	Winter s.	Before	Summer s.	Winter s.
CF1	127.61	106.36	119.515	206.44	210.165	212.86
CF2	117.47	104.995	118.255	140.32	116.58	135.05
CF3	47.73	22.27	41.115	112.62	100.14	111.79
CF4	163.71	145.64	159.54	196.92	167.45	195.585
CF5	372.63	347.355	348.48	353.94	320.815	331.91
CF6	105.62	109.22	113.14	279.84	307.02	284.73
CF7	79.46	75.99	77.595	262.60	287.185	272.975

Table 6. Breaking forces of coated fabric before and after weathering.

Sample of coated knitted f.	Average breaking force in the wale direction – F_{cw} , N			Average breaking force in the course direction – F_{cc} , N			Average breaking forces of spherical burst – F_{sb} , N		
	Before	Summer s.	Winter s.	Before	Summer s.	Winter s.	Before	Summer s.	Winter s.
CF1	1030.99	771.6	914.01	556.96	438.055	513.78	1227.45	1042.8	1047.9
CF2	387.76	313.415	395.17	639.72	522.815	652.525	700.8	580.83	654.16
CF3	149.98	86.805	138.025	117.36	64.035	107.145	128.915	86.67	108.4
CF4	147.90	98.365	139.195	120.53	71.26	112.42	92.495	69.335	85.55
CF5	291.19	179.635	238.195	250.04	170.175	223.625	150.83	105.67	124.995
CF6	411.67	302.98	418.96	201.77	138.855	175.06	433.3	369.995	421.245
CF7	516.92	410.09	508.82	251.54	162.96	224.25	622.5	535.83	576.23

drological service. The most important weather information regarding the total solar radiant exposure, temperature, relative humidity and precipitation is given in **Table 3**.

After the exposure period described, the specimens were removed from exposure and tested for changes in mechanical properties.

Determination of the tensile strength and elongation at break were performed in conformity with ISO 1421: 1998 on dynamometer Statimat-M, Techtechno, Germany [19]. A test of spherical breakage was conducted in accordance with the standard EN 12332-1:1998 Rubber- or plastic-coated fabrics – Determination of bursting strength – Part 1: Steel ball method on dynamometer Apparacchi Branca, Italy. [20].

The mass (g/m²) of the knitted fabric, polyurethane coating and polyurethane coated knitted fabric was determined

according to Standard EN ISO 2286-2:1998, in which it is determined how to separate the coating from the substrate and to weigh 5 samples with a mass per unit area of 100 cm². Measurement accuracy was 10⁻⁴, it was measured on analytical scale KERNALI 220-4, Kern & Sohn GmbH, Germany [21].

The thickness was measured according to Standard EN ISO 5084:1996 i.e. 10 measurements for each fabric type. Measurement accuracy was 10⁻² [22].

The samples were statistically analysed (descriptive statistics, hypothesis testing – t-test, regression analysis).

The surface morphology of the polyurethane topcoat on the knitted fabric was monitored by scanning electron microscopy (SEM). For surface morphology characterisation, scanning electron micrographs were taken on a MIRA\LMU Tescan (Czech Republic) at 10000x mag-

nification, about 10 images taken at different points on the fabric. Fabrics were coated with Au/Pd in a sputter coater.

Results

Results of the climatic conditions measured during the exposure are given in **Table 3**. Changes in dimensional characteristics after weathering are given in **Table 4**. Elongation properties of the coated fabric before and after outdoor natural weathering are presented in **Table 5**. Breaking forces in the coated fabric before and after weathering are presented in **Table 6**.

The t-test confirmed, with a significance level of $p < 0.05$, that the differences in breaking forces measured after winter or summer aging of samples are statistically significant, as well as the differences in thickness and shrinkage measured before and after weathering. The t-test was applied because there are pairs of results,

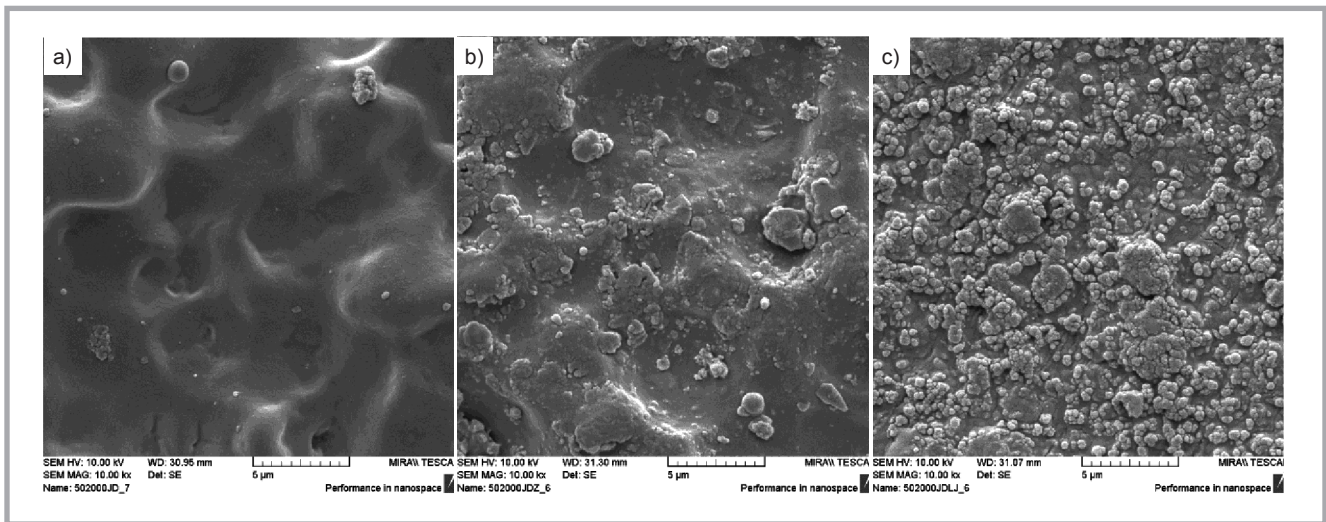


Figure 1. Surface of polyurethane layer before outdoor exposure: a) after three months of winter weathering, b) and after three months of summer weathering, c) magnification 10 kx.

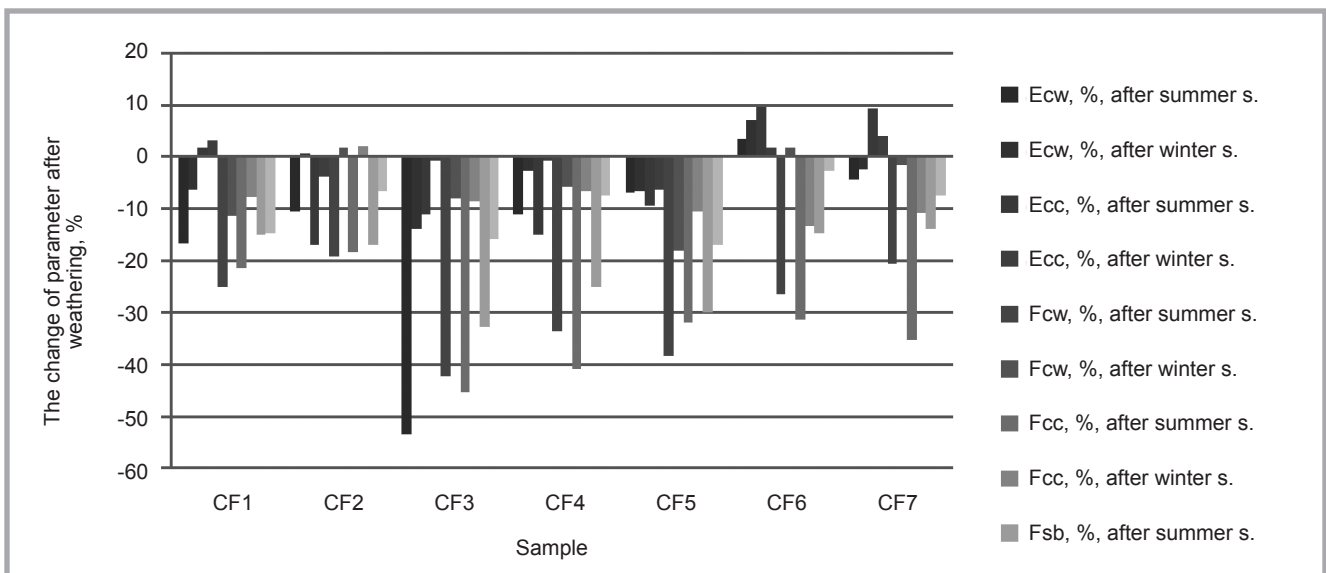


Figure 2. Change in parameters describing tensile properties after summer and winter weathering

the dependable ones, of the same samples before and after aging. Since the direction of the change was indicated, the one-way t-test was used.

■ Discussion

Modification of coated fabric dimensional characteristics after weathering

The exposure of fabrics to outdoor natural weathering caused changes in dimensional characteristics, thickness and mass, as can be seen in **Table 4**. After the weathering, the coated fabrics shrank by up to 6.5% (on average 4.3%) after the summer season, and up to 2.8% (on average 2.0%) after the winter season. They

became thinner by up to 4.8% (on average 0.5%) after the summer season, and by up to 4.8% (on average 2.4%) after the winter season. Surprisingly there are no regularities in the change of mass. Some fabrics did lose mass, and some increased in mass during both seasons, which can be attributed to the simultaneous action of the wear and abrasion of fabrics, which reduces mass, while shrinkage contributes to an increase in the mass per unit area.

Considering the effect of fabric constructional parameters on shrinkage, there was no perceived correlation between the raw material, yarn count, mass per unit area of the substrate or coated

fabric and the thickness of the substrate or coated fabrics with respect to shrinkage. During the summer season, shrinkage is higher for all fabric tested, and the fabric which experienced high shrinkage during the winter season experienced even higher shrinkage during the summer season. The correlation between the winter shrinkage and summer shrinkage of the fabric is high ($r = 0.829$). Therefore shrinkage should be attributed to degradation of the polyurethane cover. Results confirm the hypothesis that if a fabric is exposed to a higher dosage of radiation, it is likely to experience higher degradation. Generally the degree of surface degradation on all the coated fabrics should be more severe

due to the higher dosage of radiation. Partial degradation of the polyurethane layer is confirmed by scanning electron microscopy (SEM) analysis. An illustration is given for specimen CF1, as well as SEM images taken at a magnification of 10000x (10 kx) (*Figure 1*). Deterioration of the polyurethane layer caused by weather conditions is evident. Here SEM images of naturally weathered polyurethane coatings presented show blisters that are very similar to those formed after accelerated weathering in a QUV chamber [8]. It is suggested that the alternating dry and wet environment caused the formation of osmotic cells and thus blistering.

Modification of tensile properties after weathering

As seen from *Table 5*, *Table 6* and *Figure 2*, there was a significant average decrease in all parameters describing tensile properties after the exposure. Summer exposure made greater modification of every parameter measured than winter exposure. Weathering made a greater impact on the decrease in breaking forces and a lesser, but not insignificant, impact on elongation.

Modification of elongation properties after weathering

Before weathering, the coated fabric has a considerably higher average elongation in the wale direction in relation to the knitted substrate – on average about 16% (*Table 2*, *Table 5*).

The regression analysis shown in *Equation (1)*, with a high coefficient of determination $R^2 = 0.992$, indicates the relationship between the elongation of the knitted substrate and that of the polyurethane-coated fabric before weathering in the wale direction:

$$\epsilon_{cw} = 1.2312 \epsilon_{kw} - 8.4717, \quad (1)$$

where ϵ_{cw} is elongation of the polyurethane-coated fabric, and ϵ_{kw} that of the knitted substrate.

After weathering, elongation in the wale direction decreases, which was expected due to the deterioration of material; however, it is interesting to what extent the decrease occurs in polyurethane coated knitted fabric in the two different weather conditions. After the winter season, elongation in the wale direction decreases on average by 3.6%, and after the summer season by a considerable 10% on average

regarding unexposed coated fabric (*Figure 2*). This study confirms that solar radiation has great impact on the ageing of elongation properties, although on some other properties like the ageing of thermal protection, humidity had a greater impact [7].

In the course direction, the coated knitted fabric before weathering has a significantly higher average elongation in relation to the knitted fabric – on average about 102% (*Table 2*, *Table 5*).

It was previously established that by using multiple linear regressions, a good relationship could be determined between the elongation of the coated fabric and that of the knitted substrate in the course direction. Variables which significantly affect the elongation of the coated fabric in the course direction are the elongation of the knitted substrate and ratio between the knitted substrate thickness and coating thickness [2]. Using *Equation (2)*:

$$\epsilon_{cc} = 149.3042 + 2.032309 \epsilon_{kc} - 44.866 T_r, \quad (2)$$

(ϵ_{cc} = elongation of coated fabric (%); ϵ_{kc} = elongation of knitted fabric (%); T_r = thickness ratio of knitted fabric and coating), the elongation of the coated fabric can be predicted. The coefficient of multiple correlation ($R = 0.91$) indicates a strong relationship between the elongation of the coated knitted fabric in the course direction and the two variables observed.

After weathering, elongation in the course direction decreases, but scarcely. After the winter season, elongation in the course direction decreases by 0.5%, and after the summer season by 2.8% on average compared to that of unexposed coated fabric (*Figure 2*). Again the impact of solar radiation on the ageing of elongation properties is evident.

Considering the effect of fabric constructional parameters on elongation after weathering, there was no perceived correlation between the raw material, yarn count, mass per unit area of the substrate or coated fabric and the thickness of the substrate or coated fabrics and the elongation after weathering. Elongation measured before weathering and that measured after summer weathering are strongly correlated ($r = 0.995$), as well as between elongations before and after winter weathering ($r = 0.998$).

Modification of breaking forces after weathering

Before weathering, the coated fabric has considerably higher average breaking forces in the wale direction in relation to the knitted substrate – on average 24.2% (*Table 2*, *Table 6*).

The linear regression model, shown in *Equation (3)*,

$$F_{cw} = 1.098 F_{kw} + 48.736, \quad (3)$$

with the coefficient of determination $R^2 = 0.980$, explains the relationship between the occurrences observed, giving the possibility to predict the values of breaking forces in the wale direction of polyurethane-coated knitted fabric (F_{cw}) for known values of breaking forces of the knitted fabric (F_{kw}).

After weathering, breaking forces in the wale direction decreased. After the winter season breaking forces in the wale direction decrease slightly on average by 1.6%. Solar radiation has a great impact and after the summer season breaking forces decrease significantly by 26.3% on average as compared to those in the wale direction of unexposed coated fabric (*Figure 2*).

In the course direction, the coated knitted fabric before weathering has significantly higher average breaking forces compared to those of the knitted fabric – by about 27.3% on average (*Table 2*, *Table 6*). The regression model, shown in *Equation (4)*,

$$F_{cc} = 99.511 + 1.003908 F_{kc}, \quad (4)$$

with the coefficient of determination $R^2 = 0.937$, explains the relationship between the values of breaking forces in the course direction of the polyurethane-coated knitted fabric (F_{cc}) for known values of breaking forces of the knitted fabric (F_{kc}).

After weathering, breaking forces in the course direction decreased. After the winter season, breaking forces in the course direction decrease considerably by 10.8% on average, and after the summer season significantly by 35.2% on average in relation to the elongation of unexposed coated fabric (*Figure 2*). This confirms that on the ageing of breaking forces of coated fabrics, solar radiation has an even greater impact than on elongation properties.

Since the steel ball method is recommended for determination of the bursting strength of knitted fabric or other high elastic textile materials, this method was also applied. The specificity of this method is that by using a steel ball, the textile material stretches spherically, and the angles of the force on the surface of the material continuously change during material testing [23].

After coating, tensile forces increased significantly, with the coating resulting in a greater resistance to spherical breakage, on average 14.5%.

After winter weathering, the breaking forces decreased by 7.4% average, and after summer weathering by 16.8% (**Figure 2**).

Considering the effect of fabric constructional parameters on breaking forces after weathering, there are especially strong positive correlations between the thickness of coated fabric and breaking forces. For spherical breakage there is a correlation of $r = 0.903$ between the thickness and breaking forces of no weathered fabric, where $r = 0.910$ between the thickness and breaking forces of winter weathered fabric, and $r = 0.905$ between the thickness and breaking forces of summer weathered fabric.

■ Conclusions

The exposure of coated fabrics to outdoor natural weathering caused changes in all properties investigated. Summer exposure made greater modification of every parameter measured than winter exposure, except for the thickness.

The most significant changes were as follows:

- coated fabrics shrank by 4.3% on average after the summer season, and by 2.0% on average after the winter season,
- the thickness decreased by 0.5% on average after the summer season, and by 2.4% on average after the winter season,
- elongation in the wale direction decreases after the winter season by 3.6% on average, and after the summer season by a considerable 10% on average. The elongation in the course direction decreases by 0.5% after the winter season, and after the summer season by 2.8% on average,

- breaking forces in the wale direction decrease by 1.6% on average after the winter season, and after the summer season by a significant 26.3% on average. Breaking forces in the course direction after the winter season decrease by 10.8% on average, and after the summer season a significant 35.2% on average,
- breaking forces of spherical breakage decreased after winter weathering by 7.4% on average, and after summer weathering by 16.8%,
- the decrease in the breaking forces of coated fabrics due to solar radiation has a greater impact than for other properties measured.
- there is a strong positive correlation between the thickness of the coated fabric and breaking forces, which can be used to design coated fabric with better tensile properties.

It has to be taken into account that the results presented may show variability when compared with results from repeated exposures in the same location at a different time, but is important to determine the range of performance of coated fabrics made with different constructional and tensile properties.

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