Colour fading in the polyurethane coating depending on the substrate and conditions of natural weathering

Vesna Marija Potocic Matkovic, Ana Sutlovic and Martinia Ira Glogar*

University of Zagreb Faculty of Textile Technology, Zagreb, Croatia
**Email: martinia.glogar@ttf.hr*

Coated textiles are mostly used in clothing, medicine and transport. Advantages of polyurethane coatings are greater resistance to abrasion and splitting, increased strength and durability. The properties of such materials can be significantly affected by pigment dispersion. Polyurethane-coated knitted fabrics were of interest because they exhibit positive mechanical and thermal properties, and yet they are little studied. Polyurethane coating was prepared in pastes in yellow, blue and dark blue hue, which is used to obtain polyurethane coatings. The results are presented as differences in CIEL*a*b* colour parameters and total colour difference. After exposure to the natural weathering, it is noticed that in the summer season the materials in dark blue hues resist best, while in winter conditions the smallest difference in colour is obtained for yellow materials. In addition, a good correlation of knitted substrate mass, thickness and yarn count with colour fading occurred.

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Introduction

Numerous scientific studies are conducted in the field of development of coloured polymer dispersions for textile coatings. A wide range of coloured pigment paste dispersions is available for applications for a wide variety of applications which can affect the properties of the substrate in synergy. The development of coloured polymer dispersion is primarily aimed at improving the weathering resistance of usable properties such as elasticity, tensile strength or friction. The additional treatment of PUR coated (PUC) knitted fabrics can be fungus, antibacterial, antistatic and flame-retardant treatment, or agent to enhance the colour fastness. Sundang *et al.* [1] investigated PUR as dye fixing agents. Das [2] investigated the influence of UV ageing on the properties of green PUR coatings. The yellowness index (ΔYI) follows a systematic increasing trend with increment in irradiation time which indicates photodegradation of polyurethane. Štaffová *et al.* [3] studied dynamic color and phase change of chosen thermochromic systems and their incorporation into polyurethane textile coating.

The gap in the field of scientific research of the application of coloured coatings is in the textile substrate properties. Varying the structure of fabric, density, mass, thickness and yarn count it is possible to obtain a coated fabric with knitted substrate with different properties. Coated knitted fabrics are generally more stretchable and elastic than coated woven fabrics and therefore protective clothing and sportswear are more comfortable then clothes made out of coated woven fabric. Information of weather durability is essential when developing new textile materials or improving existing materials intended for outdoor use [4].

Degradation of textile material under natural weathering conditions is caused by sunlight, temperature and moisture. For handling natural exposure tests different exposure techniques are available. Proper exposure methodology, with reference to seasonal changes in weather are especially important to ensure that the test results are useful, especially for textiles. Seasonal differences greatly affect the time and mode of physio-mechanical degradation of coated textiles [4]. The ideal way to test materials which have a short service life is to expose a replicate test array at different seasons of the year. Weatherability of coated textiles was mostly researched at high loads coated fabric used in the building industry. Generally, the degree of surface degradation on all the fabrics was more severe due to the harsher climate, if a fabric is exposed to a higher dosage of UV radiation, it is likely to experience the higher degradation [5].

This paper examines the impact of natural weathering on the colour fading of PUC fabric. Research was also focused on the selection of fabric construction parameter which correlates with the colour fading best, and can serve as indicator to predict colour fading of tested knitted fabrics.

Experimental

Materials and structural properties

Nine knitted fabrics with different structures were chosen to cover a wide interval of the tested characteristics. They were coated under the same conditions, on the same coating line, with PUC from Novotex (Table 1). PUC was prepared in three colours from the base of hydrophilic polyester which is used to obtain PUC which let water vapour pass through. Polyurethane was applied to the knitted fabric using the transfer procedure. The polyurethane paste was applied to the backing paper using the pump. The paper is directly introduced through the whole coating line (Recomo Company) and is used as an endless conveyor for applying polyurethane. Coatings are adjusted with the distance between the knife on which the polyurethane paste is applied and the roller under the knife. The applied polyurethane paste with the paper passes through the dryer with speed of 10 m/min, where the temperature was adjusted to 80 °C. Here, drying is carried out due to evaporating solvent. At the dryer exit there are cooling rollers to cool down the PUC. Subsequently the other coating of the same polyurethane paste is applied in the same way. The final coating was a polyurethane binding agent on which the knitted fabric was laminated. In the dryer at 160 °C, during 3 minutes, the binder was cross linked. At the end of the coating line there is a unit to separate the backing paper from the finished material. The backing paper returns to the beginning of the coating line and is used to apply the polyurethane paste. The mass of PUC was 80 g/m^2 and thickness 0,16 mm.

Pigment dispersion suitable for the pigmentation of polyurethane in solution, for transfer or direct coating, was used. Pigments were Norene from Novotex in appearance of viscous paste in yellow, blue and dark blue colour hue.

Coated fabric sample	Knitted fabric - substrate						Coated fabric	
	Structure	Material	Yarn count (dtex)	Mass per unit area of substrate (g/m²)	Thickness (mm)	Density per cm horizontal / vertical	Total mass per unit area (g/m²)	Thickness (mm)
CF1	Simplex	PA	55	184	0,74	18/17	283	0,78
CF2	Locknit	PA	111	152	0,62	14/24	249	0,62
CF3	Power-net	PES	17	47	0,26	10/60	130	0,30
CF4	Voile	PES	17	60	0,32	12/54	147	0,40
CF5	Power-net	PA	13	134	0,4	12/68	238	0,47
CF6	Locknit	PA	44	284	0,86	28/38	385	0,88
CF7	Simplex	PA	44	167	0,65	17/15	264	0,69
CF8	Locknit	PA	44	279	0,77	28/40	372	0,78
CF9	Sleeknit	PA	13	100	0,51	13/88	192	0,51

Table 1: Properties of substrate and coated fabrics.

Measuring methods

Ageing of 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 EN ISO 877-2:2010 – Part 2: Direct weathering.

The rack employed in test was made from untreated wood; a flat frame mounted on a support was suitable. The exposure angle was fixed at 45°, facing the equator. The location of exposure was Zagreb, Croatia (lat.: 45° N, long.: 16° E), with humid continental climate with hot summers and cold winters. Duration of exposure of samples during summer season was from 15th July to 15th October, and during winter season from 1st of December to 1st of March. The climatic conditions during the test were monitored and reported by courtesy of Croatian Meteorological and hydrological service. The most important weather information is given in Table 2.

Duration of exposure	Total solar radiant exposure (J/cm²)	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)
15.07.-31.07.	12211	20,4	67	63,3	0
01.08.-30.08.	16622	23,2	61	15,6	0
01.09.-31-09.	13740	20,3	63	42,0	0
01.10.-15.10.	5305	12,5	71	26,5	0
Aver. summer	**47878**	**19,1**	**66**	**147,4**	**0**
01.12.-31.12.	6107	3,7	85	84,5	1
01.01.-31.01.	7753	2,5	72	19,4	1
01.02.-01.03.	10186	-1,9	69	26,3	27
Aver. winter	**24046**	**1,4**	**75**	**130,2**	**29**

*Table 2: The climatic conditions during the test (*Aver. – average value for season).*

The evaluation of colour characteristics has been obtained objectively using a remission spectrophotometer DataColor Spectra Flash 600 PLUS – CT. The results are presented as total colour difference values (ΔE_{CIE76}) obtained by measuring and comparing the samples before and after the samples exposure to natural weathering during summer or winter season. Colour difference values were calculated using Equation 1, defining the samples before exposure as reference samples,

$$\Delta E_{CIE76} = ((\Delta L^*)^2+(\Delta a^*)^2+(\Delta b)^2)^{1/2} \quad (1)$$

where ΔL* is difference in lightness value, Δa* and Δb* are differences in a* and b* colour coordinates indicating the change in L*a*b* colour space position and also indicating the change in chroma (C*) and hue (h).

The mass (g/m²) of the knitted fabric, without and with PUC was determined according to the standard EN ISO 2286-2:1998 for coated surface fabrics, 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.

The thickness was measured according to the standard EN ISO 5084:1996, i.e. 10 measurements for each fabric type. The obtained results were statistically analysed (descriptive statistics, hypothesis testing, regression analysis).

Discussion

Results in colour changes during weathering are shown in Table 3. While values of correlation coefficient of the constructional parameters of knitted substrate and colour fading is given in Table 4.

Samples	ΔL*	Δa*	Δb*	ΔC*	Δh	ΔE	ΔL*	Δa*	Δb*	ΔC*	Δh	ΔE
Yellow	**Summer season**						**Winter season**					
CF1	-2,53	2,89	-11,26	-10,66	-4,63	11,89	-0,42	1,92	0,05	0,32	-1,90	1,97
CF2	-2,55	3,77	-12,53	-11,73	-5,79	13,33	-0,13	2,07	0,05	0,34	-2,04	2,07
CF3	-5,27	1,70	-20,33	-19,79	-4,96	21,07	-3,16	0,12	-4,78	-4,72	-0,76	5,73
CF4	-3,70	0,92	-17,53	-17,19	-3,58	17,94	-2,07	-0,52	-3,01	-3,05	0,13	3,69
CF5	-2,85	1,95	-14,12	-13,64	-4,12	14,53	-1,26	0,27	-1,42	-1,37	-0,45	1,91
CF6	-2,74	2,38	-16,20	-15,61	-4,95	16,60	-0,25	1,57	0,42	0,63	-1,50	1,64
CF7	-2,35	1,87	-13,95	-13,49	-4,01	14,27	-2,07	-1,40	-2,99	-3,14	1,02	3,90
CF8	-4,22	1,53	-16,94	-16,49	-4,16	17,53	-0,26	2,95	0,27	0,70	-2,88	2,98
CF9	-3,01	1,46	-14,10	-13,71	-3,58	14,49	-1,25	-0,11	-2,42	-2,42	-0,20	2,73

(a)

Samples	ΔL*	Δa*	Δb*	ΔC*	Δh	ΔE	ΔL*	Δa*	Δb*	ΔC*	Δh	ΔE
Blue	**Summer season**						**Winter season**					
CF1	1,05	-8,03	5,04	-0,89	-9,44	9,54	1,15	-5,56	0,67	1,56	-5,38	5,72
CF2	1,17	-7,85	4,95	-0,91	-9,24	9,35	1,61	-5,53	0,24	1,93	-5,19	5,77
CF3	-0,92	-3,96	9,87	-7,17	-7,85	10,67	-0,25	-0,97	4,35	-3,73	-2,44	4,46
CF4	0,40	-7,80	6,32	-2,06	-9,83	10,05	0,72	-5,42	3,26	-0,79	-6,28	6,37
CF5	0,51	-8,16	5,09	-0,85	-9,58	9,63	1,31	-5,47	1,11	1,13	-5,47	5,73
CF6	1,09	-7,95	3,54	0,31	-8,70	8,77	1,07	-5,33	0,72	1,41	-5,19	5,48
CF7	0,19	-8,73	3,87	0,47	-9,54	9,55	0,92	-5,78	0,65	1,68	-5,57	5,89
CF8	1,22	-7,58	5,77	-1,74	-9,37	9,61	1,43	-5,35	0,43	1,67	-5,10	5,55
CF9	0,53	-8,49	5,28	-0,81	-9,96	10,01	0,74	-5,74	1,27	1,12	-5,77	5,93

(b)

Samples	ΔL*	Δa*	Δb*	ΔC*	Δh	ΔE	ΔL*	Δa*	Δb*	ΔC*	Δh	ΔE
Dark blue	**Summer season**						**Winter season**					
CF1	-0,22	-0,07	5,12	-5,12	0,23	5,13	-0,24	1,20	4,27	-4,15	1,57	4,45
CF2	-0,83	-1,57	4,44	-4,47	-1,47	4,78	-0,57	-0,2	3,88	-3,89	1,00	3,93
CF3	-0,1	-2,78	3,51	-3,49	-2,80	4,48	-0,19	-1,17	3,13	-3,16	-1,07	3,35
CF4	-0,16	-2,13	4,75	-4,77	-2,09	5,21	-1,16	-0,88	3,85	-3,88	-0,73	4,11
CF5	-0,18	-3,23	3,60	-3,55	-3,29	4,84	-0,25	-1,26	2,59	-2,63	-1,19	2,89
CF6	-0,74	-2,01	4,11	-4,13	-1,96	4,63	-0,97	-0,75	4,05	-4,08	-0,59	4,23
CF7	-0,29	-2,61	3,16	-3,16	-2,62	4,11	-0,73	-1,5	4,29	-4,32	-1,40	4,60
CF8	-1,36	-1,54	3,36	-3,39	-1,47	3,94	-0,63	-0,04	3,88	-3,88	0,19	3,93
CF9	0,48	-2,36	3,72	-3,73	-2,34	4,43	0,35	-0,77	2,41	-2,44	-0,68	2,56

(c)

Table 3: Colour changes between exposed and unexposed samples during summer and winter season of (a) yellow, (b) blue and (c) dark blue samples.

Parameters of coated textile	ΔL*	Δa*	Δb*	ΔC*	Δh	ΔE
	Summer season					
Yarn count of substrate	0,4195	0,8699	0,5086	0,5396	-0,7557	-0,4711
Mass per unit area (g/m²)	0,3270	0,3028	0,2484	0,2561	-0,2180	-0,2527
Thickness of substrate (mm)	0,5153	0,4526	0,4664	0,4746	-0,2595	-0,4679
Density horizontal (loops/cm)	0,1331	0,0984	0,0234	0,0275	-0,1104	-0,0311
Density vertical (loops/cm)	-0,3935	-0,5750	-0,3878	-0,4057	0,4678	0,3709
Total mass per unit area (g/m²)	0,3725	0,3275	0,2911	0,2987	-0,2204	-0,2963
Thickness (mm)	0,5368	0,4227	0,4684	0,4747	-0,2200	-0,4732
	Winter season					
Yarn count of substrate	0,6053	0,5462	0,5900	0,5961	-0,5108	-0,3821
Mass per unit area (g/m²)	0,7663	0,6529	0,8236	0,8217	-0,5862	-0,5823
Thickness of substrate (mm)	0,8002	0,5920	0,8210	0,8131	-0,5161	-0,6195
Density horizontal (loops/cm)	0,6461	0,6097	0,7064	0,7101	-0,5602	-0,4151
Density vertical (loops/cm)	-0,3374	-0,2899	-0,4188	-0,4154	0,2486	0,1598
Total mass per unit area (g/m²)	0,7804	0,6417	0,8374	0,8332	-0,5705	-0,6191
Thickness (mm)	0,7829	0,5611	0,8203	0,8095	-0,4806	-0,6315

Table 4: Values of correlation coefficient of the constructional parameters of knitted substrate and colour fading after summer and winter season.

Weathering of yellow samples during the summer season given in Table 3 show the most significant change in colour (ΔE>11) with the largest change occurring in the chromaticity value (ΔC*>-10). The most important influence of the sun is proved by ΔE<4 during the winter season. Samples show that changes in colour and lightness are correlated (Table 4) with the mass and thickness of the knitted substrate, and thus with the mass and thickness of the PUC textile. After exposing the PUC knitted textiles to summer conditions, the colour changes are larger but also less correlated with the substrate. Greater exposure to solar radiation has a greater impact than the properties of the substrate. Blue samples, especially dark blue have a more uniform colour fading throughout the year (Table 3). Blue PUC samples in colour and lightness values correlate with the mass and thickness of the substrate (Table 4). Correlations in colour changes are higher in winter but correlations in brightness are higher in summer. Dark blue PUC textiles show very small changes in colour during winter without correlations, in summer it can be seen more noticeable changes and correlations.

In addition to the characteristics of textile substrates, these changes are the result of polyurethane and pigment chemistry. Polyurethane polymers are made by combining isocyanates (R-N=C=O) with polyols containing hydroxyl (-OH) functional groups. Coloured polyurethane is result of interaction of functional groups with the pigment in dispersion form. Weathering of polyurethane polymer causes degradation in the direction of reducing mechanical properties and chemical degradation as well. Both of these changes result in colour fading. In addition, during exposure to atmospherics, pigment degradation occurs, first on the azo group which is more typical for yellow pigments.

Conclusions

Presented investigation of coated fabric fading and its dependence on fabric substrate, as well as environmental conditions, give a good insight into the behaviour of coated fabrics. PUC fabrics are widely used for different outdoor purposes, and therefore exposed to natural weathering that may intensively affect the fading. The information about the intensity of fading should be useful when projecting coated materials in order to improve fabric properties.

The investigation outlined that in addition to the previously established dependence of colour fading on the choice of polymer and colour pigment, this study established the relationship between fading and the substrate itself on which the coloured polyurethane coating is deposited.

Changes in colour and lightness are correlated with the mass and thickness of the knitted substrate, and thus with the mass and thickness of the PUC textile. After exposing the PUC knitted textiles to summer conditions, the colour changes are larger but also less correlated with the substrate.

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