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CHANGES IN CELLULOSIC MATERIALS FROM HERITAGE TEXTILES DURING AGEING TREATMENTS

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Abstract

This paper examines and compares the thermal stability and mechanical changes during hygrothermal weathering of cellulosic materials, like those found in heritage textile collections. The influence of fibre type and fibre content was evaluated using TGA and DTA measurements, as well as tensile tests for different natural fibres: cotton, flax and hemp. The results of this study may help researchers choose the most appropriate conservation treatment for each textile collection.

Keywords: flax, hemp, artificial ageing, thermal analysis, tensile tests

1. Introduction

Museums across the country house valuable, yet vulnerable collections of ethnographic textiles. The storage and conservation of historical textiles raises many challenges, due to the inherent instability of the different natural fibres induced by the action of combined deterioration agents [1, 2]. These agents affect textile heritage artefacts determining discoloration, changes in appearance, loss of strength and increasing of elongation, partial or complete destruction of the material with underlying chemical changes, such as oxidation state, degree of polymerization, and breakdown of molecular structure. The effect of chemical and physical damage due to the natural aging process is influenced also by the raw material manufacturing techniques. The artificial aging method, which simulates the effect of natural climate factors like temperature, ozone and light (UV rays), is widely used to study the aging process of textiles.

Cellulose is the main constituent of vegetable fibres from textile materials. In order to examine the extent of degradation of textile material, published studies made use of analytical techniques such as: spectral methods [3-6], thermal analysis [6-10], determination of the degree of polymerization of the

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natural polymer [7], X-ray diffraction [11] and mechanical tests [12].

The results of our study will provide a better understanding of the aging process of various cellulosic materials (cotton, flax and hemp). Although the natural fibres that were used in the study consist mostly of cellulose, the fibres also contain various percentages of hemicelluloses, lignin, pectins, waxes and proteins (Table 1).

Table 1. Chemical composition of some natural fibres [14].

Type of fibre	Content (%)					
	Cellulose	**Hemicelluloses**	**Lignin**	**Pectins**	**Waxes**	**Proteins**
Cotton	90 – 94	8.5 – 4.5	-	-	0.5	-
Flax	71 – 76	22.3 – 17.3	2.2	2 - 5	3.5	2.0 – 5.0
Hemp	74 - 77	18.4 – 15.4	3.7	4 - 8	4.0	0.5 – 1.0

2. Experimental part

2.1. Fibres

The hygrothermal aging experimental models were designed using woven fabrics made from 100% cotton, 100% flax and 100% hemp. Their basic characteristics are shown in Table 2.

Table 2. Main properties of the woven fabrics.

Woven fabrics made from	Thickness (mm)	Warp density (threads/10cm)	Weft density (threads/10cm)
cotton	0.373	240	170
flax	0.707	160	140
hemp	1.108	150	150

2.2. Weathering procedure

The cotton, flax and hemp woven fabrics were submitted to the following hygrothermal ageing conditions: the temperature was set at 40^0C and the relative humidity was set at 65 %. All samples were kept in these conditions for 24 hours (V_1), 48 hours (V_2) and 120 hours (V_3) in a laboratory chamber (Angelantoni Ind., Italy).

2.3. Analytical techniques

2.3.1. Thermal analysis (TGA, DTA)

Thermal analysis was used for the prediction of material stability under the specified conditions. A Mettler Toledo instrument was used to analyze the thermal decomposition of the fibres. The samples were heated in nitrogen environment, at a constant rate of 10ºC per min, using a steady flow of 20

mL/min over a temperature range of 25÷600ºC. The TGA dynamic curves, as well as the DTG curves recorded for all samples had been analyzed in order to evaluate the effect of the fibre type on the degradation process of the sample.

2.3.2. Tensile tests

After the hygrothermal ageing treatment, some yarns were extracted from the fabric structure and there were analyzed the main tensile properties: breaking force (N) and relative elongation or deformation to rupture (%). Both properties were measured on the *TINIUS OLSEN H5KT* dynamometer, accordingly to ISO 2062 standard.

3. Results and discussion

3.1. Thermal stability

The thermogravimetric characteristics of the fibres and the time derivative of the mass fraction (DTG) curves were examined. Analytical results obtained for the untreated cotton, flax and hemp samples are presented in Table 3. The determination of kinetic parameters for the thermal decomposition reaction, namely the activation energy (Ea), pre-exponential factor (lnk0) and reaction order (n) employed the difference – differential model developed by Freeman-Carroll [14] and are also included in Table 3.

Although all the samples showed one-stage decomposition, the main components (hemicelluloses, cellulose and lignin) in the cellulosic textiles induced a slight different change under high temperature conditions. It was found that the structure property of the three components have a complex influence on the course of chemical reactions of the natural polymers [15].

Table 3. Thermogravimetric data and kinetic parameters of the nitrogen pyrolysis reaction for unaged samples of cotton, hemp and flax.

Sample series	Thermal degrad. steps	T_i (°C)	T_{max} (°C)	T_f (°C)	W (%)	Residue	Ea (kJ/mol)	n	lnk_0
cotton	I	327	361	382	80.46	19.54	217.53±0.16	0.77±0.00109	36.61±0.0312
flax	I	301	360	377	77.35	22.65	196.6±0.92	0.57±0.00808	32.53±0.18
hemp	I	320	359	384	78.88	21.12	292.35±0.59	1.07±0.00364	51.27±0.11

Ti – initial temperature of mass loss; Tmax – temperature of maximum reaction rate; Tf – final temperature; W – mass loss, Ea – activation energy; n – reaction order; lnk_0 – pre-exponential factor

TGA/DTG curves for cotton fabric in Figure 1a showed a decrease in the weight of the sample of about 5% during the increase of temperature from 58 to 105°C, corresponding to a loss of water from the cellulose sample. Cellulose further decomposed through the formation of levoglucosan (1,6-anhydro-β-d-glucopyranose) and its subsequent decomposition mechanisms: C-O bond breaking, direct C-C bond breaking, and dehydration [16].

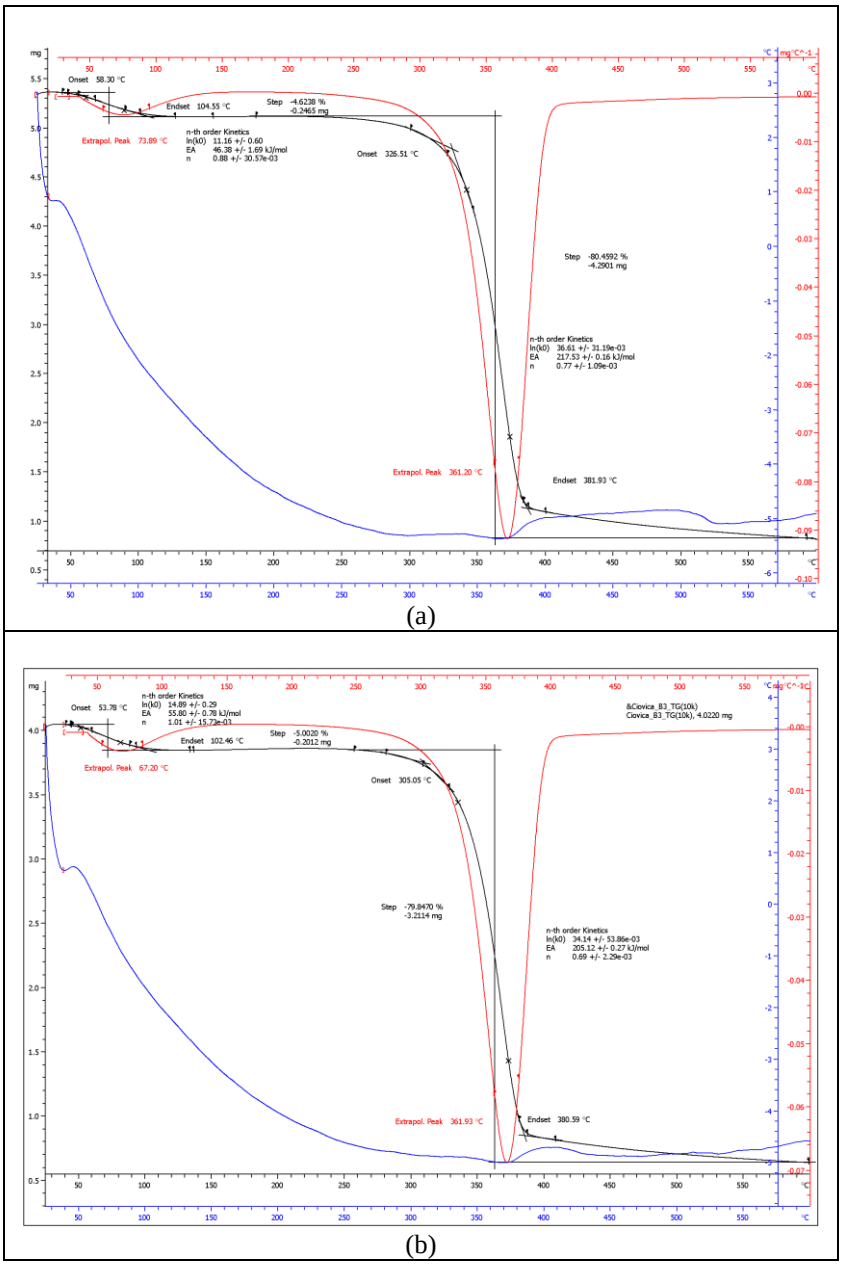

Figure 1. TGA/DTG curves for the cotton samples: (a) untreated and (b) aged for 120 h.

The process began at 327°C and a large endothermic peak of cellulose, at 361°C, appeared in the temperature range corresponding to the rapid weight loss. The results are consistent with those from other studies, which showed that pure cellulose pyrolysis takes place at a higher temperature range than pyrolysis of cellulose with hemicelluloses and lignin (see Table 3) [15].

For the cotton sample subjected to weathering for 120 hours, a slight reduction of the thermal stability is indicated by the lower value for the onset temperature Ti = 305 °C. This is also confirmed by the kinetic parameters: the activation energy (Ea) is decreasing from 218 kJ/mol to 205 kJ/mol during the accelerated aging process. In both derivative curves, the degradation reaction reached the maximum value for about 361± 1°C. For the mass loss and the char residue formation no significant changes are marked during weathering at 40°C and 60% relative humidity.

Data in Table 3 indicate that hemp also decomposes in one step, but behaved differently from cellulose-containing cotton, due to lignin and hemicelluloses content. TGA indicates that hemp lost about 4% of its weight due to evaporation until it reached 320°C; during the successive heating runs, further loss of sample mass was observed. The temperature at which the reaction rate reached its maximum value of degradation was 359°C in the derivative curve. This step was related to a mass change of 79 %.

Thermal degradation profile and stability of the flax sample in the nitrogen atmosphere showed differences from cotton and hemp samples. Degradation began at lower temperature (301°C), the onset temperature was recorded at 360°C, and occurred slowly within the whole temperature range until the end of the pyrolysis at 377°C, seemingly due to lignin that usually degrades over a wide range of temperature [15].

The thermal stability of cotton is generally better than that of hemp and flax containing lignocelluloses and hemicelluloses (Table 3), since lignocellulosic fibres start to degrade at a lower temperature than cellulose. The weight loss values in hemp and flax during the experiments reflect hemicelluloses and lignin degradation versus heating time in a nitrogen environment. Cellulose gives a lesser amount of residues, whereas lignocellulosic fibres can form from 21 to 23 wt% of chars.

Although DTG curves of textile samples were qualitatively similar to each other, the activation energy for the pyrolisis reaction and the reaction order both for hemp and flax are different from the cotton sample pyrolysis, thus indicating a different pattern in the thermal degradation reaction.

3.2. Mechanical changes

3.2.1. First stage of processing the experimental data

In the first stage it was applied a *one-way analysis of variance (ANOVA)*. This method is used to examine the relationship between a response numeric variable (a tensile property) and a factor of influence (the aging treatment). For each type of analyzed fibres and for each tensile property, we tested the following null hypothesis (H_0) compared to an alternate hypothesis (H_1):

H_0: the population means are equal (i.e., the aging treatment does not have a significant effect on the variable)

H_1: the population means are not equal (i.e., the aging treatment has a significant effect on the variable)

For this analysis, we considered four levels of the factor (q = 4), encoded V0 (a standard woven fabric with no treatment), V1, V2 and V3, as described above. For each level of the factor, there were n = 10 experimental data, therefore the we used a total of 240 experimental data for the analysis (4 levels of aging factor x 10 experimental data for each level x 3 types of fibres x 2 tensiles, the total number of data in the preliminary table was N = 40). In conclusion, in the preliminary stage there were processed 40 x 3 types of fibres x 2 tensile properties = 240 of experimental data.

Table 4. ANOVA results for the cotton yarns.

Breaking force, N						
Source of variation	***SS***	***DF***	***MS***	***FC***	***F***	***Conclusion***
Exterior	39.674	3	13.225	151.226	2.87	**H_o is rejected**
Interior	3.148	36	0.087			
Total	42.822	39	1.098			
Elongation, %						
Source of variation	***SS***	***DF***	***MS***	***FC***	***F***	***Conclusion***
Exterior	2.007	3	0.669	5.149	2.87	**H_o is rejected**
Interior	4.678	36	0.130			
Total	**6.685**	**39**	**0.171**			

Table 5. ANOVA results for the flax yarns.

Breaking force, N						
Source of variation	***SS***	***DF***	***MS***	***FC***	***F***	***Conclusion***
Exterior	4928.87	3	1642.957	267.346	2.87	**H_o is rejected**
Interior	221.24	36	6.145			
Total	5150.11	39	132.054			
Elongation, %						
Source of variation	***SS***	***DF***	***MS***	***FC***	***F***	***Conclusion***
Exterior	1.929	3	0.643	2.90	2.87	H_o is rejected
Interior	7.98	36	0.222			
Total	**9.91**	**39**	**0.254**			

For the ANOVA procedure we computed three values necessary for Fisher test for every source of variation: sum of squares (SS), degrees of freedom (DF) and mean of squares (MS). The computed value (FC) was then

compared with a nominal Fisher value (F) read at 0.95 probability and degrees of freedom 3 and 36. If the value FC > F, H_0 was rejected and H_1 was accepted with the probability of 0.95 [17].

The results for cotton, flax, and hemp yarns are shown in Tables 4-6.

Table 6. ANOVA results for the hemp yarns.

Breaking force, N						
Source of variation	***SS***	***DF***	***MS***	***FC***	***F***	***Conclusion***
Exterior	4353.80	3	1451.266	64.540	2.87	**H_o is rejected**
Interior	809.51	36	22.486			
Total	5163.31	39	132.392			
Elongation, %						
Source of variation	***SS***	***DF***	***MS***	***FC***	***F***	***Conclusion***
Exterior	6.60	3	2.200	6.826	2.87	H_o is rejected
Interior	11.60	36	0.322			
Total	18.20	39	0.467			

Hypothesis H_1 was accepted with 0.95 probability in all cases. The population means computed for V_0, V_1, V_2 and V_3 are not equal. In conclusion, the tensile properties (i.e., breaking force and elongation) of all cellulosic yarns are influenced by the aging treatment.

3.2.2. Second stage of processing the experimental data

During the second stage of the experiment, we compared the loss of strain resistance and the increase of elongation in the cellulosic yarns extracted from the woven fabrics with standard textile materials which received no aging treatment (V_0).

Table 7. Experimental means for breaking force and elongation.

		V_0	**V_1**	**V_2**	**V_3**
Breaking force, N	Cotton yarn	2.551	2.461	2.334	2.011
	Flax yarn	27.960	27.081	26.215	22.812
	Hemp yarn	25.712	25.304	24.548	21.895
Elongation, %	Cotton yarn	2.917	2.967	2.985	3.470
	Flax yarn	3.324	3.568	3.629	3.940
	Hemp yarn	3.773	4.079	4.165	4.881

Table 7 summarizes the means values for breaking force (N) and elongation (%) for the three types of cellulose fibres. Table 8 presents the computed values for loss of strain resistance (%) and for the increase of elongation (%) taking in consideration the standard yarns in each category. The

comparison of the tensile properties of the cellulosic yarns is shown in Figures 2 and 3.

Table 8. The evolution of tensile properties for treated yarns.

		V_0	V_1	V_2	V_3
Loss of strain resistance, %	Cotton yarn	-	3.53	8.51	21.17
	Flax yarn	-	3.14	6.24	18.41
	Hemp yarn	-	1.59	4.53	14.85
Increase of elongation, %	Cotton yarn	-	1.69	2.32	18.96
	Flax yarn	-	7.35	9.16	18.53
	Hemp yarn	-	8.11	10.40	29.37

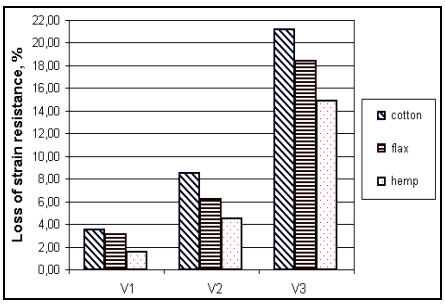

Figure 2. Comparison between cellulosic yarns regarding the loss of strain resistance, %.

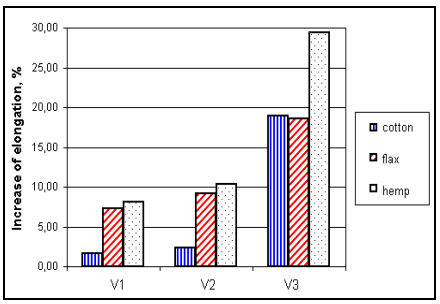

Figure 3. Comparison of cellulosic yarns regarding the increase of elongation, %.

4. Conclusions

- The results of this study add to the previous knowledge pertaining to effect of fibre type on the thermal and mechanical properties for three common cellulosic fibres (cotton, flax and hemp) found in ethnographic textile materials.
- The main components (cellulose, hemicelluloses and lignin) and the supermolecular structure in the cellulosic textiles give the pattern of thermal degradation of the fibres, which indicates that lower lignin content improves thermal stability.
- The effect of the accelerated aging treatment upon tensile properties of cellulosic yarns made from cotton, flax and hemp is influenced by the fibre type.
- After 24 hours of treatment, the cotton fabric was mostly affected – the loss of resistance for the yarns was 3.53% on average (Figure 3). The situation was the same after 48 hours, when cotton yarns lost 8.51% of their breaking force – the biggest value, and also after 120 hours of treatment, when it was computed 21.17% loss. As for the increasing in elongation, cotton fabrics

were greatly deteriorated after 120 hours of treatment (V_3) when this parameter reached 18.96%.

- The flax yarns have a medium change during the aging process. Their loss of resistance is between cotton and hemp for all variants (V_1, V_2 and V_3). The maximum value is 18.41% registered after 120 hours of treatment. Their elongation increased slowly and remained on the last place at V_3 (18.53% is lower than cotton and hemp).
- The hemp yarns were thicker than cotton and flax yarns. Also the woven fabric had the biggest thickness of all three samples and had the higher density both in warp and weft directions. These may explain the changes observed in the hemp yarns during the aging process (Figure 3). The elongation increased because of the humidity absorption by hemp fibres, reaching the highest value 29.37% at V_3.

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