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Physical and Chemical Characterization of Cellulose Based Textiles Modified by Periodate Oxidation

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Summary: Conversion of dihydroxyl groups to dialdehyde by periodate oxidation is a useful method widely used in derivatization of cellulose to activate the polymer to further reactions as grafting polymerization. To investigate the cellulose behavior at different level of oxidation and to better understand the influence of the crystallinity on the effects induced by oxidative reactions on different cellulose materials, linen and cotton textiles have been oxidized with periodate solutions in different conditions. Oxidized cellulose samples have been characterized by several techniques: solid-state ^{13}C NMR, Wide Angle X-Ray diffraction, and SEM. Moreover the mechanical properties of the untreated and oxidized yarns have been evaluated by means of tensile tests, the oxidation degree has been measured by means of the hydroxylamine hydrochloride method.

Keywords: cellulose; fibers; graft copolymers; oxidation; textiles

Introduction

The main component of the most important natural textiles, flax and cotton, is the cellulose, a not-branched polymer of glucose, linked through 1,4-β-glucosidic bonds. The number of repeating units in the chain is variable and constitutes the degree of polymerization (DP). This value depends on the nature of the native plants and on the type of treatments used

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during the spinning, the weaving and the finishing processes. The mechanical properties of a cellulose-based fiber, such as its tensile strength, are largely dependent on its DP.[1]

The main reactions acting on the structure of cellulose and causing the alteration of textiles are photo-degradation, acid hydrolysis, oxidation and biodegradation. A complete analysis of them is quite complex, since these phenomena are all related to each other.

To better understand the reactions related to the natural oxidative ageing of the textiles, in the present paper we would describe the effect of an artificial oxidation process carried out with sodium methaperiodate. Methaperiodate oxidation is a highly specific reaction to convert dihydroxyl groups in two aldehydic groups, without significant secondary reactions;[2] the reaction cleaves the C2 - C3 bond. The resulting compound is the dialdheyde cellulose DAC. The glucosidic bond becomes weaker: with the depolymerization the mechanical strength of the material get worse.[3] Moreover yellowing of the material is observed, owing to the formation of chromophores, able to absorb UV-Visible radiations. In this study samples of dialdheyde cellulose from linen and cotton with different oxidation degrees was prepared and characterized by solid-state ^{13}C CP-MAS NMR spectroscopy, Wide Angle X-Ray diffraction, Scanning Electron Microscopy and evaluation of the mechanical properties by tensile tests. To evaluate the oxidation degree induced by methaperiodate a new, very fast and simple technique was used. The DAC was converted in the correspondent nitrogen-containing compound (oxime), by Schiff base reaction with hydroxylamine hydrochloride.[4] The aim of our work is to obtain a model to investigate the natural ageing of real materials with the same level of degradation of the artificially oxidized samples. In order to recover the mechanical properties of the degraded cellulosic textiles, the naturally and artificially oxidized fabrics can be consolidate by means a new method: the grafting polymerization of acrylic polymers.[5-7] The results of this research will be published in a future extended paper.

Experimental Part

The cellulosic samples used in our research were natural linen “Artemisia” and cotton “Ghinea”, supplied by Zecchi, Florence, Italy. Textiles were oxidized without preliminary treatments of deffating, since any additives were present. All the reagents were laboratory grade products from Aldrich, used without further purification. To investigate the cellulose behavior at different level of oxidation, two different solutions of sodium methaperiodate

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were used: 0.1 M and 0.4 M. The ratio sample/solution was kept for all experiments 1g of sample for 100 ml of solution. The treatments were carried out for different times of reaction:

- Linen: 1, 2, 4, 6, 8, 24, 72 h
- Cotton: 1, 2, 4, 6, 8, 24, 72, 120 h

The residual weight % and the linear density for all the oxidized samples were measured.[8] The determination of the aldehyde content in the DAC samples were performed as described in a previous paper.[9] The physical-chemical characterization of linen, cotton and of their oxidized samples was performed by a solid state ^{13}C CPMAS NMR study.[10] This method allows calculating the amounts of the amorphous component and of oligomers due to depolymerization process of cellulose during the oxidation, as described in a previous paper.[7]

WAXS intensity profiles for cotton, linen and the oxidized samples have been collected by means of a PW 1060/71 Philips Diffractometer (Cukα Ni-filtered radiation) equipped with a sample holder for sample spinning. High voltage was 40 KV and tube current was 30 mA. A standard sample was employed to determinate the instrumental broadening.

Tensile tests were carried out on cotton, linen an their oxidized yarns following the standard ASTM D2256-97. Uniaxial tensile tests were performed by means of an Instron 5564 tensile testing machine operating with a cross-head speed of 20 mm/min at 25 °C. Before testing samples were conditioned according to the standard UNI EN 20139. For each sample, at least 15 yarns were tested, to access the reproducibility. Cotton and linen yarns, untreated and oxidized, were observed by means of a Philips XL20 Scanning Electron Microscope. The samples were mounted on carbon coated stubs and observed at 30 KeV.

Results and Discussion

Periodate oxidation of cellulose is a complex process, since it proceeds gradually from the amorphous to the crystalline phase; prolonged reaction times and higher oxidant concentrations could be necessary to access into the inner region of the polymer.

In this study several oxidations with different oxidation time and different concentration of methaperiodate solution were carried out. As foreseen, increasing the reaction time and the methaperiodate concentration, the textiles degrade more extensively, loosing weight: in strong conditions ($NaIO_4$ 0.4 M for 72 h) linen looses the 70 % of it initial weight and cotton the 30 %. Actually higher concentrations of the oxidant solution reduce the time necessary to reach a greater degree of oxidation. The oxidation modifies the aspect of textiles, which become stiffer and brittle; when the oxidation conditions are very strong, textiles show a yellowing-brownish color. The oxidation leads to a shrinkage of yarns; this effect can be evaluated by Linear Density (LD) measurements, according to the standard UNI EN ISO 1973. The values obtained for untreated samples are 85.5 tex and 37.7 tex respectively for linen and cotton. By increasing the oxidation time and the $NaIO_4$ concentration, LD increases to 161.8 tex for linen oxidized for 48h with $NaIO_4$ 0.1 M and to 64.3 tex for cotton oxidized for 120 h with $NaIO_4$ 0.1 M. The oxidation on cotton and linen involves different results; particularly, in the same conditions, linen undergoes aging phenomena stronger than cotton, as confirmed by the FTIR spectroscopy.[9] This fact could be due to the presence of lignin, that catalyzes the oxidative degradation in the dark. Following the Tappi Test T222 om-88 it is possible to evaluate the amount of lignin in a cellulose based material; in linen the lignin is present (about 3 %) but not in cotton. The aldehydic content in the DAC samples was been determined by transformation of DAC in nitrogen-containing derivative by reaction with hydroxylamine hydrochloride. By elemental analysis the nitrogen content of each sample was calculated. This value is directly related to the aldehydic groups, because the oximation reaction is quantitative. By a simple equation, the moles of carbonyl groups per 100 g of cellulosic samples and their number per 100 glucose units were found. Increasing the oxidation time, the number of aldehydic groups rises for both the textiles for every methaperiodate concentrations used, as described in a previous paper.[9] Moreover, the values obtained show that the time necessary to reach a greater degree of oxidation is reduced increasing the oxidant concentration. Either a stronger oxidation (i.e. linen oxidized with $NaIO_4$ 0.4 M for 24 h) introduces a number of aldehydic groups per 100 glucose units rather low, even if the sample looks very degraded. This result can be explained if we suppose that the methaperiodate oxidation, in stronger conditions, leads to break not only the pyranose ring, but also the 1,4-β-glucosidic bonds along the cellulose chain. The CP-MAS ^{13}C NMR analysis confirms this effect, showing an amount of oligomers, derived from the chain breaking. In figure 1a the ^{13}C CP-MAS NMR spectrum of linen is shown together with the full assignment of all cellulose resonances. The resonances labeled with a “c” are due to the crystalline domains, while the broad resonances labeled with an “a” are due to amorphous environment. In figure 1b, c, d and e the spectra of linen after 4, 8, 24 and 48 hours of oxidation with $NaIO_4$ 0.1 M are

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shown. Spectra of oxidized samples show an evident broadening. The broadening of the resonances is mainly due to the formation of oligomers compounds, resonating in 90-100 ppm range, and to the increase of cellulose amorphous components, as shown by the increase of the signal at 84 and 63 ppm due to C4a and C6a respectively. Increasing the oxidation time, a progressive broadening of resonances is observed. A characteristic features is the lack of the carbonyl signal due to the dialdehyde compound, expected at about 200 ppm, even at high oxidation degree. In fact due to the formation of aldehyde in hemiacetal species, these aldehyde compounds are difficult to characterize by NMR techniques. Increasing the oxidant concentration from 0.1 to 0.4 M, the spectra show considerable changes even at shorter oxidation time. In figure 1f, g and h the ^{13}C CP-MAS spectra of linen after 2, 6 and 24 hours of oxidation with $NaIO_4$ 0.4 M are shown. In this case the degradation of cellulose structure is more evident: after 24 hours a full degradation is observed. A full spectral deconvolution allows the evaluation of the amount of oligomers and amorphous component; ratios between the area of resonances due to the carbon 4a and 4c and between the area of resonances due to carbon 6a and 6c were calculated and the ratio between the area of resonances due to oligomers and the area of carbon 1 due to cellulose were reported in table 1. The data confirm that, increasing the oxidation, the amorphous and oligomer components progressively rise. Analogous analysis was carried out on cotton samples. An oxidation treatment of cotton with $NaIO_4$ 0.4 M for 24 hours gives results similar to the one obtained by treatment with $NaIO_4$ 0.1 M for 120 hours. Comparing the spectra obtained for linen in the same oxidation conditions, it can be observed that the cotton samples undergo a milder degradation. In linen, oxidized with a methaperiodate solution 0.1 M, 24 hours of treatment are sufficient to obtain a large amount of amorphous component and oligomer samples well comparable to that obtained for cotton with an oxidation treatment of 120 hours. WAXS intensity profiles collected for cotton and linen (see figure 2) samples exhibit the well resolved spectrum of Cellulose I or Native with the three characteristic reflections (101), $(10\bar{1})$ and (002); the first two are of medium strong (ms) intensity and highly convoluted each other, in the range between 13 and 18 degrees of 2θ and the third, almost totally resolved, very sharp and with an extremely strong intensity (vvs), at 22.8 degrees of 2θ. From these figures it can be observed that Cellulose I profiles are shown also by oxidized cotton and linen samples; moreover the

Cellulose I profiles become less resolved at increasing the concentration of methaperiodate, for fixed time of oxidation, and at increasing time of oxidation, for fixed concentrations.

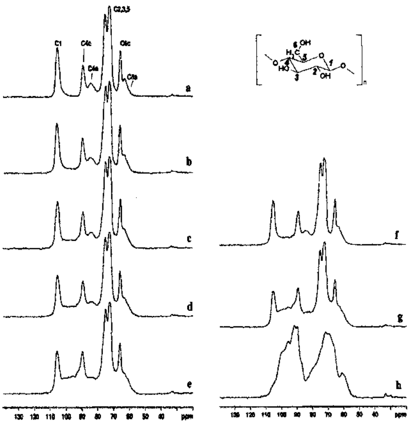

Figure 1. ^{13}C CP-MAS NMR spectra of linen: a) unaged linen; b) linen oxidized with $NaIO_4$ 0.1 M for 4 h ; c) 0.1 M, 8 h; d) 0.1 M, 24 h; e) 0.1 M, 48 h; f) linen oxidized with $NaIO_4$ 0.4 M for 2 h; g) 0.4 M, 6 h; h) 0.4 M, 24 h.

Table 1. Results of ^{13}C NMR spectra deconvolution for linen and cotton.

Time ox (h)	Linen				Cotton			
	0.1M		0.4M		0.1M		0.4M	
	C4a/C4c	C1 olig/ C1 cell	C4a/C4c	C1 olig/ C1 cell	C4a/C4c	C1 olig/ C1 cell	C4a/C4c	C1 olig/ C1 cell
0	0.9 ± 0.1	0	0.9 ± 0.1	0	0.8 ± 0.1	0	0.8 ± 0.1	0
2	-	-	1 ± 0.1	0.4± 0.08	-	-	0.9 ± 0.1	0.2 ± 0.02
4	0.9 ± 0.1	0.1± 0.01	-	-	0.8 ± 0.1	0.3 ± 0.1	-	-
6	-	-	1.8 ± 0.2	1.4 ± 0.2	-	-	1.0 ± 0.1	0.6 ± 0.1
8	1.4 ± 0.1	0.4± 0.08	-	-	-	-	-	-
24	1.6 ± 0.3	0.6± 0.13	-	-	1.4 ± 0.1	0.5 ± 0.1	2.1 ± 0.2	1.8 ± 0.3
48	4.8 ± 0.2	1.4 ± 0.2	-	-	-	-	-	-
120	-	-	-	-	2.1 ± 0.3	1.2 ± 0.2	-	-

Crystallinity index of Cellulose I was evaluated according to the Segal method, using the following relationship: $X_c = (I_{002} - I_{18°}/I_{002}) * 100$

where I_{002} is the intensity of the 002 reflection, in arbitrary units, and $I_{18°}$ is the diffraction intensity, in the same units, at 18 degrees of 2θ, the angle corresponding to the maximum in the WAXS intensity profiles of a completely amorphous cellulose.

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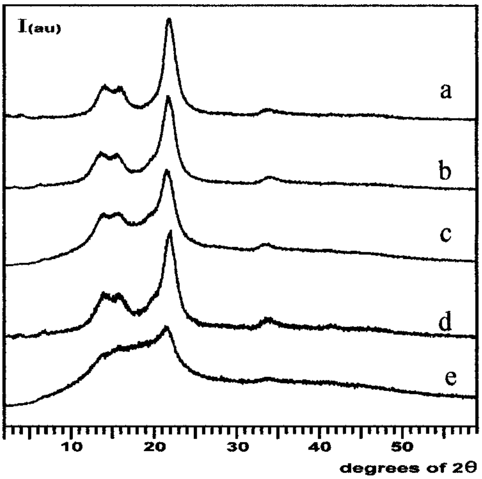

Figure 2. WAXS intensity profiles of linen samples: a) untreated linen; b) linen oxidized with $NaIO_4$ 0.1 M for 4 h; c) 0.1M for 48 h; d) linen oxidized with $NaIO_4$ 0.4 M for 2 h; e) 0.4 M for 24 h.

X_c values obtained for cotton and linen samples are reported in table 2. These data show that the crystallinity indexes of Cellulose I in cotton fabrics are higher than in linen fabrics. After oxidation X_c values decrease in both cases and this decreasing is correlated, at fixed time of oxidation, with the concentration of the oxidizing agent; at fixed concentrations, with the oxidation times. Moreover it is interesting to note that, for each specified methaperiodate concentration and for each time of oxidation, cotton fabrics show a value of crystallinity index higher than that exhibited by linen fabrics. The average crystal dimensions were evaluated according to the Scherrer equation: $D_{hkl} = K\lambda/\beta_0 \cos \theta_{hkl}$

where β_0 is the half-width in radiants of the reflection corrected for the instrumental broadening; λ is the wavelength of the radiation used and k is a shape factor.

Nevertheless, since the diffraction profile of imperfect crystals is affected by the lattice distortions, the $1/\beta_0$ value for the 002 reflection ($1/A_{002}$) measured in degrees of 2θ was chosen as a relative index to determine cellulose crystal dimensions. The values of $1/A_{002}$, reported in table 3 respectively for cotton and linen samples, decrease at increasing both the concentration of the oxidizing agent and the oxidation time. Despite these values it can be concluded that the crystal dimensions are not strongly affected by the oxidation process.

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Table 2. Results of X-Rays analysis for linen and cotton.

Time ox (h)	Linen				Cotton			
	0.1M		0.4M		0.1M		0.4M	
	X_c	$1/A_{002}$	X_c	$1/A_{002}$	X_c	$1/A_{002}$	X_c	$1/A_{002}$
0	0.79	0.613	0.79	0.613	0.83	0.704	0.83	0.704
2	-	-	-	-	-	-	0.77	0.662
4	0.75	0.571	0.69	0.568	0.78	0.680	-	-
6	-	-	0.60	0.562	-	-	-	-
8	0.69	0.546	-	-	-	-	-	-
24	0.61	0.532	0.24	0.518	0.73	0.658	0.54	0.625
48	0.55	0.513	-	-	-	-	-	-
120	-	-	-	-	0.58	0.649	-	-

In table 3 tensile properties data respectively for linen and cotton are reported. Specific Stress at Maximum Load (σ) and Young's Modulus (E) are normalized with respect to linear density in order to be independent from the specimen dimensions.

Cotton oxidized with sodium methaperiodate 0.1 M loses the 40 % of specific stress and the 60 % of Energy at Break after four hours of treatment. The tensile properties do not change after further 24 hours of oxidation time. After 120 hours it can be observed a strong increase of the linear density, due to the shrinkage of the yarns and a further loss of specific stress and specific Energy at Break. Moreover this sample shows an increase of the strain at maximum load and a decrease of specific Young's Modulus. Oxidation with 0.4 M methaperiodate solution shows a faster tensile properties loss. After only two hours the tensile properties values are comparable with the respective ones of cotton oxidized for 24 hours at 0.1 M. Treatments carried out for 6 and 24 hours produce a severe specific stress loss, until around 30% of the initial value.

Table 3. Tensile properties of linen and cotton yarns.

Time ox (h)	Linen				Cotton			
	0.1M		0.4M		0.1M		0.4M	
	σ (cN/tex)	E (cN/tex)	σ (cN/tex)	E (cN/tex)	σ (cN/tex)	E (cN/tex)	σ (cN/tex)	E (cN/tex)
0	31.3± 5.1	339 ± 34	31.3± 5.1	339 ± 34	10.9± 0.4	149 ± 14	10.9±0.4	149 ± 14
2	-	-	6.6 ± 0.9	174 ± 38	-	-	6.9 ± 0.6	134 ± 11
4	12.7± 1.6	395 ± 44	-	-	6.4 ± 1.0	112 ± 14	-	-
6	-	-	0.7 ± 0.1	11 ± 3	-	-	3.7 ± 0.2	61 ± 4
8	9.4 ± 1.0	296 ± 28	-	-	-	-	-	-
24	3.0 ± 0.6	53 ± 12	-	-	6.2 ± 0.8	109 ± 15	3.7 ± 0.5	15 ± 3
48	1.4 ± 0.2	15 ± 4	-	-	-	-	-	-
120	-	-	-	-	4.1 ± 0.3	28 ± 4	-	-

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Tensile properties of untreated linen yarns exhibit higher values with respect to cotton; in fact, among cellulose derived fibers, linen is well known for its very good mechanical properties. However after only 4 hours of treatment with $NaIO_4$ 0.1 M specific stress at maximum load changes from the initial value of 31.3 cN/tex to 12.7 cN/tex, with a loss of the 60 %, just like the cotton after 120 hours, and its specific Energy at Break is reduced of more than 80 %. But even after this high mechanical degradation, the process is clearly not complete: specific stress at maximum load considerably decreases increasing the oxidation time. After 48 hours of treatment we observe that specific stress at maximum load is reduced to 1.4 cN/tex. After 24 hours of oxidation time, linen shows a great decreasing of Young's Modulus in comparison with the less oxidized samples. Treatment with $NaIO_4$ 0.4 M leads to a more rapid degradation; after only 2 hours of oxidation, the specific stress value is 6.6 cN/tex and after 6 hours is still further reduced to 0.7 cN/tex. Linen oxidized for 24 hours undergoes a so deep structural damage that no tensile properties evaluation is possible.

SEM micrographs of untreated and oxidized cotton and linen are reported in figures 3 and 4. In the untreated cotton (figure 3a) the morphological characteristics of cotton fibers are well visible: the fibers appear as flat band with convolutions along their entire length. Figures 3b and c report representative SEM micrographs of cotton oxidized for 24 hours respectively with a 0.1 M and a 0.4 M methaperiodate solutions. It is interesting to observe, particularly in figure 3c, a higher number of convolutions, compared to the untreated cotton, and the presence of crimps. These phenomena are probably responsible for the shrinkage of the yarns observed for highly oxidized cotton. In fact after 24 hours of oxidation with a 0.4 M methaperiodate solution, cotton yarns show a reduction in its length of about the 40 %. The evidence of these crimps can explain also the strong decrease in the specific stress at maximum load and Young's Modulus for highly oxidized cotton yarns.

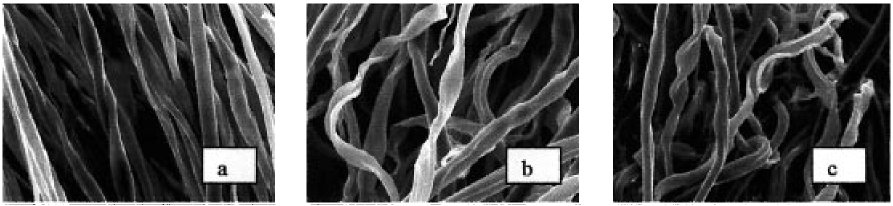

Figure 3. SEM micrographs of: a) untreated cotton fibres; b) oxidized cotton fibres with $NaIO_4$ 0.1 M for 24 h; c) oxidized cotton fibres with $NaIO_4$ 0.4 M for 24 h.

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In figure 4a untreated linen fibers are shown; the so-called bamboo structure is well evident; fibers appear as straight, stiff cylinders with nodes along their length. The oxidized fibers present a phenomenon of bending, which involves just some fibers at low oxidation level (figure 4b) and almost all fibers at higher oxidation level (figure 4c). It is also interesting to observe carefully linen after 24 hours of oxidation with 0.4 M methaperiodate solution: the morphological features of linen fibers are no more visible, particularly the nodes that make it similar to a bamboo cane, and the swelling of the fibers is clearly evident (figure 4c).

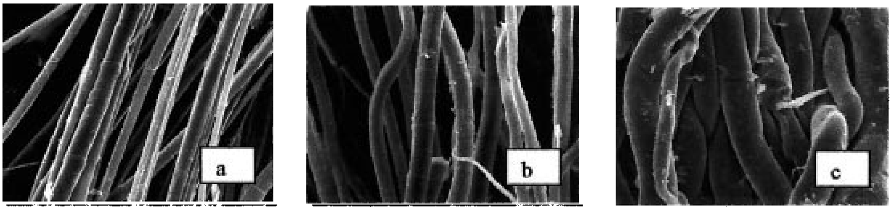

Figure 4. SEM micrographs of: a) untreated linen fibres; b) oxidized linen fibres with NaIO$_4$ 0.1 M for 24 h; c) oxidized linen fibres with NaIO$_4$ 0.4 M for 24 h.

Conclusions

The studies here reported give an insight in understanding the structural changes occurring when cellulosic textiles are oxidized and in explaining the correlation between structural changes and physical properties, such as mechanical properties and shrinkage of textiles, observed after oxidation by sodium methaperiodate. The oxidation reaction involves different results on linen and cotton. The textile oxidation depends on the reaction time and on the concentration of oxidant agent. However, the oxidation process is stronger for linen than cotton; such evidences are confirmed by all analytical techniques used to characterize textiles. Likely the presence of lignin only in linen aids its greater degradation in comparison with cotton, because lignin becomes a catalyst for this aging.

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