

STRUCTURAL CHANGES IN HEMP FIBERS FOLLOWING TEMPERATURE, HUMIDITY AND UV OR GAMMA-RAY RADIATION EXPOSURE

ANGELICA OLARU*, TEODOR MĂLUȚAN**, CRISTINA MARTA URSESCU*
MARIA GEBA* and LACRAMIOARA STRATULAT*

*“Moldova” National Complex of Museums, 1, Stefan cel Mare Blvd., 70028 Iasi, Romania

**“Gh. Asachi” Technical University, Faculty of Chemical Engineering and Environmental Protection, 73, Dimitrie Mangeron Blvd., 70050 Iasi, Romania

✉ Corresponding author: Angelica Olaru, angelicaolaru66@yahoo.com

Received August 4, 2014

This paper aims at assessing the behavior of hemp fibers when subjected to a hydrothermal treatment (40 °C, 60% RH), followed by exposure to UV radiation for 120 and 500 hours or to different doses of gamma-rays (10 and 25 kGy). Attenuated total reflectance Fourier transform infrared spectroscopy (FTIR-ATR) and X-ray diffraction (XRD) were employed to estimate crystallinity changes. The combined action of temperature, humidity, and UV or gamma-ray radiation resulted in structural changes in the lignocellulosic material, in correlation with the time of exposure to UV or the absorbed dose of ionizing radiation. The resulting data can be useful in heritage conservation for selecting the most appropriate storage or display conditions (temperature, humidity, light) for lignocellulosic textile collections, or in the case of a disinfection treatment that uses ionizing radiations.

Keywords: hemp, FTIR-ATR, XRD, crystallinity, gamma radiation, conservation

INTRODUCTION

In preserving items of historical value, a good conservation policy for cellulosic textiles is not only about protecting against the risks caused by environmental factors, but also about the use of appropriate methods of conservation, requiring scientific substantiation of optimal treatment interventions.

Lignocellulosic materials (flax, hemp) form the basis of numerous ethnographic textiles from museum collections. Changes due to the action of external factors (temperature, humidity, light) within museums, which are involved in natural aging of organic materials and textiles in particular, need a long time for observation. Therefore, simulations of the main transformations through hydrothermal aging tests and combined treatments (temperature, humidity and exposure to UV radiation) are used in studying the chemical mechanisms of aging. Also, a proper conservation strategy of artifacts on lignocellulosic materials entails not only to assess the causes that influence the natural aging process, but also to study the consequences of the conservation treatments applied, such as the

disinfection of artifacts by exposure to ionizing radiation (gamma radiation). According to some studies, the recommended doses are of 0.5 kGy as insecticide and of 10 kGy as fungicide.¹⁻¹⁰

The evaluation of changes in the structure of cellulose in natural hemp fiber composition has involved the exposure of model samples to controlled conditions of temperature and humidity, followed by exposure to UV radiation, respectively exposure to ionizing radiation (gamma rays). To estimate the treatment effects on the structure of the lignocellulosic material, methods, such as ATR-FTIR spectroscopy and X-ray diffraction (XRD), which are recommended by studies in the field, were used.^{1,2,7,10,11-22}

IR spectroscopy provides extensive opportunities in the investigation of changes in the functional groups of cellulose during the various treatments applied.^{14,18,20,22-29}

In the study of cellulosic materials, the degree of crystallinity is of particular interest in explaining the processes occurring during the treatments applied. In the supramolecular organization of cellulose, highly ordered

crystalline regions join less ordered amorphous areas, and the crystalline/amorphous ratio affects the cellulose behavior in a chemical reaction (its reactivity) and the physicochemical characteristics.^{14,30,31} The evaluation of chemical accessibility for the hemp textiles subjected to hydrothermal treatment and irradiation was performed using X-ray diffraction technique (XRD). Changes in the crystallinity of cellulose-based materials were found following the variation of the crystallinity index.

EXPERIMENTAL

Materials and methods

The study was carried out on reference woven fabrics made of unprocessed hemp (marked H). The textile samples subjected to hydrothermal treatment (40 °C, 60% RH), combined treatment (action of temperature, humidity and UV) and irradiation treatments at two doses of gamma radiation (10 and 25 kGy) were analysed.

Hydrothermal treatment

Samples of hemp fibers were placed in a laboratory chamber (Angellantoni Ind., Italy) and exposed to the hydrothermal treatment. The climatic conditions were set at: 40 °C temperature and 60% relative humidity. The samples were kept for 0, 24, 48 and 120 hours, and labeled H0, H1, H2, and H3 according to the time of exposure.

Hydrothermal and UV exposure

Another set of samples was exposed both to hydrothermal conditions and UV radiation, using artificial light emitted by a mercury lamp (200< λ <700 nm, incident light intensity: 39 mW cm⁻²). The samples were kept under these conditions for 120 h (labeled H3_UV) and for 500 h (labeled H4_UV) and then removed, analyzed and compared with reference samples.

Gamma-ray exposure

The samples were irradiated at the Technological Irradiation Center IRASM/IFIN-HH, Magurele, Ilfov, Romania, using an SVST Co-60/B type irradiator. The applied doses were 10 and 25 kGy, with a dose uniformity of $D_{max}/D_{min} = 1.14$. The reference samples and the hydrothermally treated and irradiated samples were labelled according to hydrothermal exposure and irradiation doses: H0_10, H0_25, H3_10, H3_25.

FTIR-ATR spectroscopy

Structural changes in the lignocellulosic materials were monitored by attenuated total reflectance infrared (FTIR-ATR) spectroscopy, using a Bruker Vertex 70 FTIR spectrometer, equipped with ATR device (ZnSe crystal). 64 scans were acquired with a spectral resolution of 2 cm⁻¹.

X-ray diffraction (XRD)

XRD patterns of the materials were recorded using wide angle X-ray diffraction. The X-ray diffraction (XRD) diagrams were recorded on a Bruker D8 Advance X-ray diffractometer in Bragg-Brentano configuration, equipped with NaI scintillation detector and filtered with CuK α radiation ($\lambda = 1.5406 \text{ \AA}$) in 2 θ range of 5-40° at a scan rate of 2°/min. The X-ray tube was operated at 30 kV and 36 mA.

RESULTS AND DISCUSSION

FTIR-ATR spectroscopy

To assess the degradation processes of the cellulosic materials studied, their FTIR spectra were recorded before and after hydrothermal treatment and irradiation. Spectra analysis for the hemp cellulose materials tested allowed qualitative interpretation of the main structural changes (changes in the structure of the functional groups of molecules of organic compounds) due to hydrothermal degradation and under the influence of UV and gamma radiation.

Changes in the FTIR spectra recorded during the hydrothermal treatment (40 °C temperature, 60% humidity) are shown in Figure 1 (spectral area 500-2000 cm⁻¹). The IR spectra present absorption bands situated in the characteristic frequency regions of cellulose.^{26,31} The presence of lignin is evidenced by the existence of characteristic bands situated around 1590-1600 cm⁻¹.

From the analysis of the IR spectra recorded for hemp textiles subject to hydrothermal treatment, it can be noted that the considered environmental factors do not affect the molecular structure of the cellulose chain, as evidenced by the position of the characteristic bands of the functional groups in β -D-glucopyranose units of the linear polymer. There are no significant differences in the spectral curves, not even when the treatment duration increased to 120 h. The degree of structural organization was assessed by using the Total Crystallinity Index (TCI), the Lateral Order Index (LOI) and the Hydrogen Bond Intensity (HBI), the values being obtained using the relations:

$$TCI = A_{1372}/A_{2900};$$

$$LOI = A_{1420}/A_{896};$$

$$HBI = A_{3308}/A_{1330}$$

where: A_{1420} , A_{1376} , A_{2900} , A_{896} , A_{3308} , A_{1336} are the intensities of absorbance for the corresponding peaks in the ATR spectra at 1420, 1372, 2900, 3308, 1330 and 896 cm⁻¹.

The evolution of the IR parameters calculated for the hemp textiles subjected to hydrothermal treatment as a function of the treatment duration is shown in Figure 2.

With the increasing duration of the hydrothermal treatment, the crystallinity (TCI) and the lateral ordering (LOI) indices decrease, due to the different accessibility of the crystalline and amorphous characteristic areas and of the main chemical components (cellulose, hemicellulose and lignin). The presence of hemicelluloses (18.4-15.4%)^{32,33} increases the

structural availability of the hemp textile materials, because they are amorphous structural components.

It appears that hemp materials need a period of adjustment to the storage environment factors (temperature, humidity). This stage lasts approx. 24 h-48 h, after which the cellulose structure undergoes a relaxation through the reorganization of H bonds to the secondary and tertiary level. No significant changes of the structural accessibility are seen with an increase in the treatment time up to 120 h.

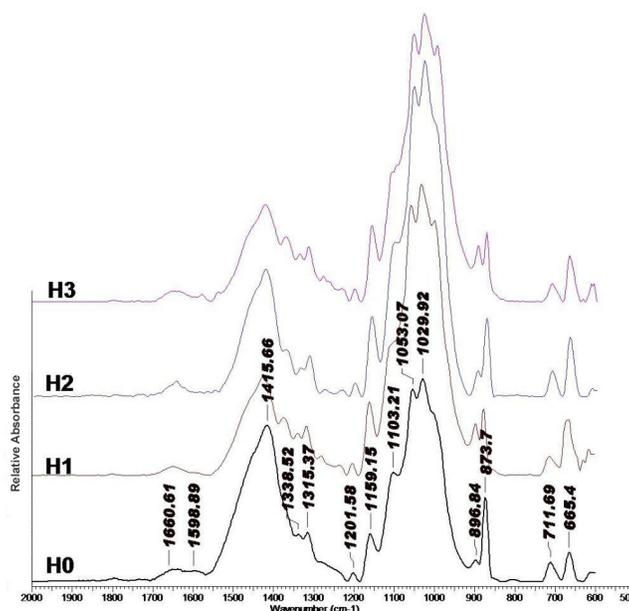


Figure 1: ATR-FTIR spectra for hemp samples (reference and samples exposed to hydrothermal treatment)

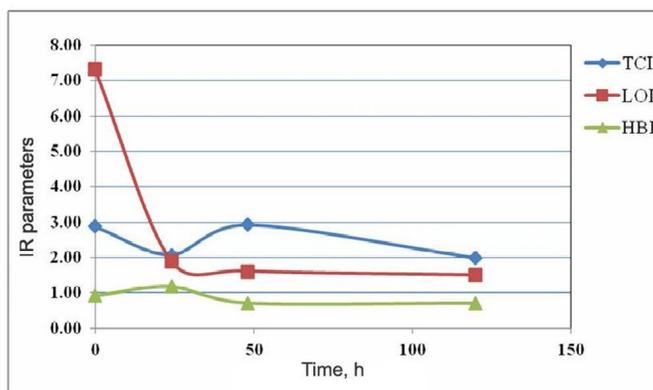


Figure 2: Infrared crystallinity ratio (TCI, LOI) and hydrogen bond intensity (HBI) of hemp samples during hydrothermal treatment

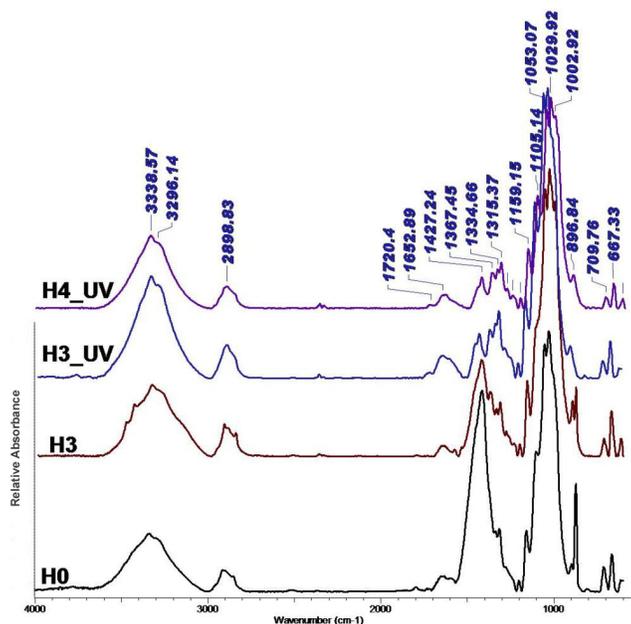


Figure 3: ATR-FTIR spectra for hemp samples

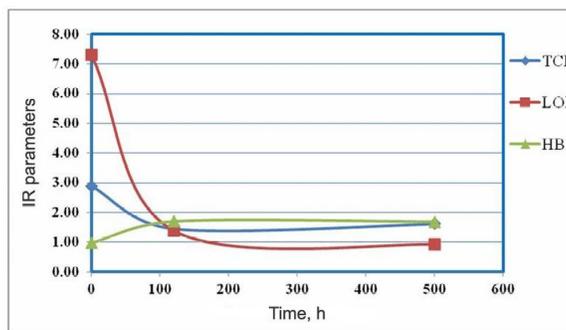


Figure 4: Infrared crystallinity ratio (TCI, LOI) and hydrogen bond intensity (HBI) of hemp samples during hydrothermal and UV exposure

In the case of the treatment combining hydrothermal and UV exposure, there are significant changes in the intensity of the infrared absorption bands (Figure 3). These changes lie in the strong decrease in LOI from 7.3 to 1.38 and in total crystallinity index TCI from 2.88 to 1.45 during the combined treatment for a period of 120 h. With continued treatment up to 500 h, there is no further significant decrease in TCI and LOI indices (Figure 4). On the contrary, the intensity of H bonds (HBI) marks an increase in the range 0-120 h followed by the stabilization of this value (Figure 4).

For exposure to gamma radiation doses of 10 and 25 kGy, the IR spectra analysis of the

samples (Figures 5 and 6) indicated a significant change in the intensity of IR absorption bands. The intensity of the band at 1416 cm^{-1} , characteristic of OH groups involved in H bonds from the crystalline areas, drops approx. 3-fold, with a shift to 1427 cm^{-1} , at the 10 kGy irradiation dose.

There is a decrease in the degree of ordering LOI of the reference sample (H0) from 7.3 to 1.88 and of the total crystallinity index TCI from 2.88 to 1.74 upon the treatment with irradiation at a dose of 10 kGy. Upon 25 kGy irradiation, there is an improvement in the degree of lateral ordering LOI and a reduction of the total degree of crystallinity TCI (Figure 7). The intensity of H

bonds (HBI) grows throughout the range of radiation doses.

On the contrary, for the hemp textile materials hydrothermally treated (H3) and then irradiated (H3_10, H3_25), the lateral ordering TOI increases for both radiation doses used, and the

total degree of crystallinity TCI records a maximum at a radiation dose of 10 kGy, and then drops to 1.23 (Figure 8). The intensity of H bonds (HBI) records a decrease in values over irradiation, as compared to the reference hemp textiles (H0).

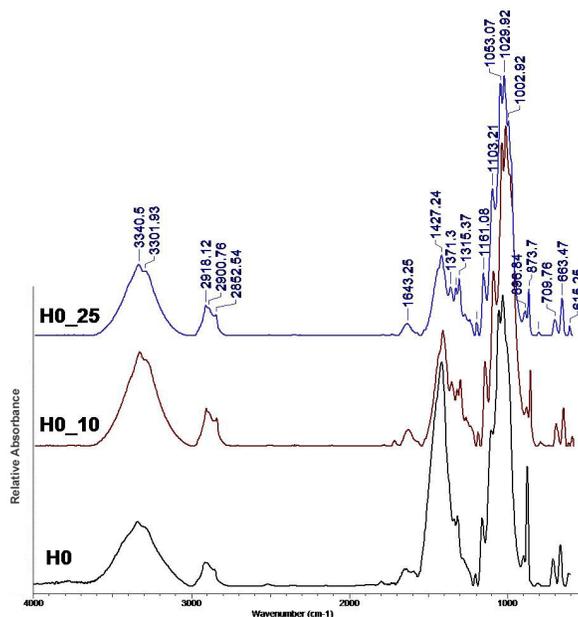


Figure 5: FTIR spectra of the hemp reference samples during gamma ray exposure

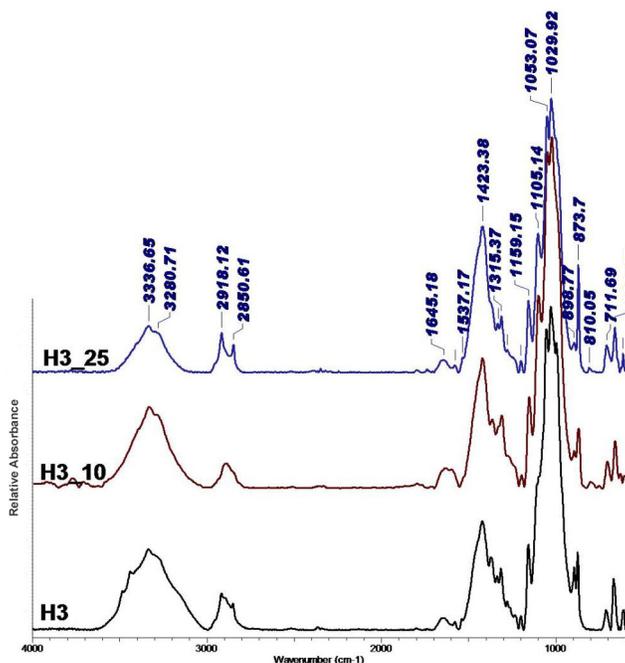


Figure 6: FTIR spectra of the hemp textiles hydrothermally treated during gamma ray exposure

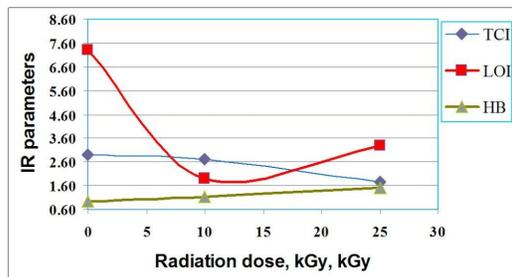


Figure 7: Infrared crystallinity ratio (TCI, LOI) and hydrogen bond intensity (HBI) for hemp reference samples during gamma ray exposure

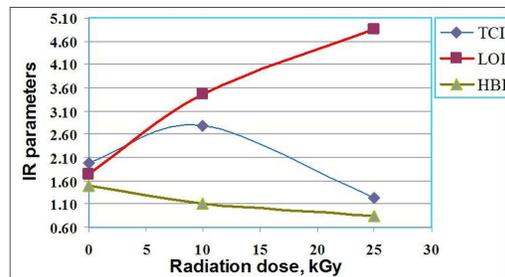


Figure 8: Infrared crystallinity ratio (TCI, LOI) and hydrogen bond intensity (HBI) for hemp after hydrothermal and gamma ray exposure

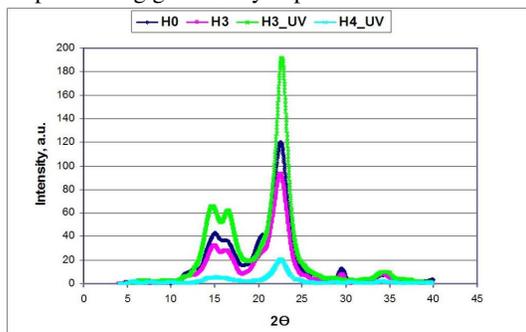


Figure 9: XRD diffraction patterns of hemp samples hydrothermally treated and exposed to UV

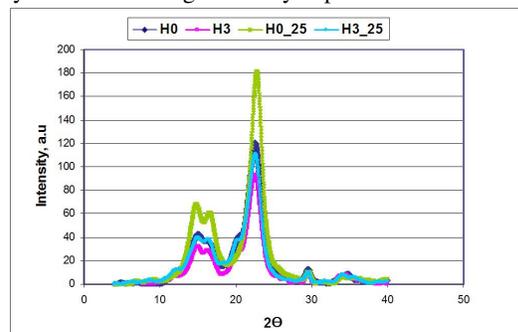


Figure 10: XRD diffraction patterns of hemp samples hydrothermally treated and exposed to gamma rays

The behavior of hemp textiles can be explained by the structural organization of these textile fibers, in terms of supramolecular organization and alternating amorphous and crystalline areas of the crystalline structure of cellulose.

It appears that through the hydrothermal treatment applied the structural accessibility of cellulose and the number of active centers available for the formation of hydrogen bond networks increase. Through the irradiation of these materials,³⁴ lateral ordering increases, which is explained by the opening of amorphous areas for the access of reactants into the cellulose structure.

These conclusions are correlated with the evolution of crystalline parameters determined by processing the diffractograms obtained by X-ray diffraction (XRD).

X-ray diffraction (XRD)

In order to assess the reactivity and accessibility of textiles subjected to hydrothermal treatment and irradiation, the X-ray diffraction technique (XRD) has been used. Changes in the crystallinity of cellulose-based materials were highlighted observing the evolution of the crystallinity index. These values were obtained

from the diffractograms recorded for the hydrothermally treated samples, and for the samples hydrothermally treated and exposed to UV and gamma ray radiation. Additionally, to characterize these changes, the contributions of each crystallographic plane to the crystallinity index and crystallite size for the studied celluloses were calculated.

Cellulose has a characteristic X-ray diffraction pattern, quite poor in reflections, in which the position and intensity of the diffraction planes are influenced by the nature of the cellulosic material and the treatment it was subjected to. Three planes in the crystalline lattice are present in the X-ray diffraction spectra of cellulose, designated as (002), (101) and (10 $\bar{1}$). The plane (002) includes the glucopyranose links forming the macromolecular chain; containing the highest density of electrons, it is the most intense and most pronounced in the diffraction spectrum. Planes (101) and (10 $\bar{1}$) correspond to hydrogen bonds between macromolecular chains; plane (101) contains more OH groups than the plane (10 $\bar{1}$), thus being more hydrophilic.²⁴

Figure 9 and Figure 10 illustrate the evolution of crystallinity, highlighted in the diffraction pattern and recorded during hydrothermal treatment and exposure to UV or gamma

radiation.

The crystallinity index values for the reference samples (H0), the samples hydrothermally treated for 120 h (H3) and exposed to UV light 120 h (H3_UV), 500 h (H4_UV), along with those for the samples irradiated with 25 kGy gamma rays, are shown in Table 1. The crystalline network parameters are shown in Table 2.

During the hydrothermal treatment, there is an increase of cellulose crystallinity from 64% to 72.6%. The same trend is recorded for hydrothermal and UV combined exposure (64-67%). These results can be attributed to the reorganizing hydrogen bond networks within the

crystalline and amorphous areas, in the case of the hydrothermal treatment, when there are changes in crystallite size planes (101) (see D_{101}) and $10\bar{1}$ (see $D_{10\bar{1}}$). Hydrothermal and UV light exposure (120 h) also causes rearrangements in the (002) plane (intramolecular hydrogen bonds), with the crystallite size increasing from 4.84 nm to 5.85 nm. On the contrary, the combined treatment prolonged to 500 h causes the destruction of the crystalline organization of the cellulose with a strong decreasing effect on the crystallinity (Figure 8).

Table 1
Cellulose crystallinity variation for hemp samples during hydrothermal treatment and exposure to UV and gamma radiation

Applied treatment	Crystallinity index					
	Reference (H0)	120 h (H3)	120 h (H3_UV)	500 h (H4_UV)	25 kGy (H0_25)	120 h, 25 kGy (H3_25)
Hydrothermal	64.05 / 85.69*	72.66 / 90.10			-	-
Hydrothermal and UV		-	67.09 / 88.85*	34.30 / 30.81*		
Gamma ray exposure	64.05 / 85.69*	-	-	-	71.51 / 90.07*	60.11 / 82.82*

* values calculated by the Segal method

Table 2
Crystalline network parameters for cellulose in hemp textiles

Sample	$\alpha(101)$	$\alpha(10\bar{1})$	$\alpha(002)$	$\alpha(101)/\alpha(10\bar{1})$	D_{101} , nm	$D_{10\bar{1}}$, nm	D_{002} , nm
Hydrothermal treatment							
H0 – reference	10.21	5.82	42.44	1.75	4.74	6.86	4.84
H3 – 120 h	11.39	7.79	48.27	1.46	5.30	5.86	4.74
Hydrothermal and UV treatment							
H3_UV – 120 h	12.78	9.69	41.29	1.32	4.41	5.44	5.85
H4_UV – 500 h	6.38	3.47	18.57	1.83	4.37	4.55	4.79
Gamma ray exposure (25 kGy)							
H0_25	14.16	10.35	43.65	1.37	4.49	5.44	5.42
H3_25	10.35	6.73	38.78	1.54	4.68	6.56	4.84

The changes of crystallinity caused by the hydrothermal treatment and gamma irradiation, and highlighted in the diffraction patterns for hemp, are shown in Figure 9. The crystallinity index values for the reference samples (H0), the samples hydrothermally treated for 120 h (H3) and irradiated with a dose of 25 kGy (H0_25, H3_25) are shown in Table 1, and the crystalline network parameters in Table 2.

A 25 kGy dose gamma irradiation results in an increase of the crystallinity for the reference sample from 64% (H0) to 71.5% (H0_25), similar

to the effect of the hydrothermal treatment, namely an increase of cellulose crystallinity from 64% to 72.6%. In the case of the samples hydrothermally treated (H3), the exposure to a dose of 25 kGy causes a decrease of the crystallinity from 72% to 60%. These results can be attributed to the reorganization of hydrogen bonds networks within the crystalline and amorphous areas in the case of the combined hydrothermal and irradiation treatment, when there are changes in crystallite size planes (101) (see D_{101}) and $10\bar{1}$ (see $D_{10\bar{1}}$).

With an evident reduction in the crystallinity index (to 34.3%), the combined hydrothermal and UV (500 h) exposure causes a much stronger destruction of the crystalline organization of the cellulose, as compared to the combined hydrothermal and gamma ray exposure.

CONCLUSION

FTIR spectroscopy reveals that although hemp textiles are affected by the hydrothermal treatment, the combined hydrothermal and UV exposure, as well as by exposure to gamma radiation, gamma radiation caused less significant degradation in cellulose structures, as compared to hydrothermal and UV (500 h) exposure. The latter treatment affected the networks of intra- and intermolecular H bonds, while exposure to radiation doses up to 10 kGy had a less evident effect. The behavior can be explained both through cellulose organization at the secondary, supramolecular and crystalline levels, as well as through formation of some macro-radicals in the cellulose chains. These are likely to induce a subsequent degradation when the combined hydrothermal and UV treatment time increases to 500 h, or cross-linking in the crystalline or amorphous regions during shorter time of exposure, inducing an apparent increase in crystallinity. There is an increase in the structural accessibility of cellulose and in the number of active centers available for the formation of hydrogen bond networks through hydrothermal treatment. Due to gamma irradiation, lateral ordering increases, which can be explained by the opening of amorphous areas to the access of reactants into the structure of cellulose.

The investigations through X-ray diffraction (XRD) confirmed that the hemp textile materials are affected by the hydrothermal treatment conditions, as well as by UV or gamma ray exposure.

Based on the data resulting from X-ray diffraction and FTIR spectroscopy analyses, textile materials such as those under study here are to be kept far from prolonged UV exposure, and if they are subjected to a gamma irradiation treatment, the recommended dose must be lower than 10 kGy.

ACKNOWLEDGEMENTS: Part of this work was supported by the Romanian Executive Agency for Higher Education, Research, Development and Innovation Funding (UEFISCDI) through the project TEXLECONS,

Improvement of Occupational Environment Quality in Cultural Heritage Deposits. Validation of Gamma Irradiation Treatment of Textile and Leather Cultural Goods, PN-II-PT-PCCA-2011-3-1742, contract no. 213/2012

REFERENCES

- ¹ E. Takacs, L. Wojnarovits, J. Borsa, C. Földváry, P. Hargittai *et al.*, *Rad. Phys. Chem.*, **55**, 663 (1999).
- ² A. K. Saha, P. Rath, D. Bhatta, *IJFTR*, **25**, 271 (2000).
- ³ M. E. Gonzalez, A. M. Calvo, E. Kairiyama, *Rad. Phys. Chem.*, **63**, 263 (2002).
- ⁴ J. Borsa, T. Toth, E. Takacs, P. Hargittai, *Rad. Phys. Chem.*, **67**, 509 (2003).
- ⁵ G. Magaudda, *J. Cult. Herit.*, **5**, 113 (2004).
- ⁶ M. da Silva, A. M. L. Moraes, M. M. Nishikwa, M. J. A. Gahi, M. A da Alencar *et al.*, *Int. Biodeter. Biodegrad.*, **57**, 163 (2006).
- ⁷ E. Bratu, I. V. Moise, M. Cutrubinis, D. C. Neagu, M. Virgolici, *Nukleonika*, **54**, 77 (2009).
- ⁸ M. E. F. Abdel-Haliem, M. F. Ali, M. F. Ghalya and A. A. Sakra, *J. Cult. Herit.*, **14**, 45 (2013).
- ⁹ W. Machnowski, B. Gutarowska, J. Perkowski and H. Wrzosek, *Text. Res. J.*, **83**, 44 (2013).
- ¹⁰ M. H. J. van der Sluijs, J. S. Church, *Text. Res. J.*, **83**, 197 (2013).
- ¹¹ Gh. Rozmarin, H. A. Schneider, D. Rusei, M. Darânga, A. Stoleriu *et al.*, *Celuloză și Hârtie*, **46**, 35 (1997).
- ¹² Th. Măluțan, A. Pui and P. P. Obrocea, *Celuloză și Hârtie*, **51**, 17 (2002).
- ¹³ M. M. Rizzo, L. D. B. Machado, S. I. Borrelly, M. H. O. Sampa, P. R. Rela *et al.*, *Rad. Phys. Chem.*, **63**, 259 (2002).
- ¹⁴ H. Kasprzyk, K. Wichlacz, *Acta Sci. Pol. Silv. Colendar. Rat. Ind. Lignar.*, **3**, 73 (2004).
- ¹⁵ F. Khan, S. R. Ahmad, E. Kronfli, *Biomacromolecules*, **7**, 2303 (2006).
- ¹⁶ V. Mamleev, S. Bourbigot J. Yvon, *J. Anal. Appl. Pyrol.*, **80**, 151 (2007).
- ¹⁷ E. Corradini, E.M. Teixeira, P.D. Paladin, J.A. Agnelli, O. Silva *et al.*, *J. Therm. Anal. Calorim.*, **97**, 415 (2009).
- ¹⁸ D. Ciolacu, F. Ciolacu, V. I. Popa, *Cellulose Chem. Technol.*, **45**, 13 (2011).
- ¹⁹ K. Kavkler, N. Gunde-Cimerman, P. Zalar, A. Demsar, *Polym. Degrad. Stabil.*, **96**, 574 (2011).
- ²⁰ L. Bilkova, *Polym. Degrad. Stabil.*, **97**, 35 (2012).
- ²¹ I. V. Moise, M. Virgolici, C. D. Neagu, M. Manea, M. Alexandru, *et al.*, *Rad. Phys. Chem.*, **81**, 1045 (2012).
- ²² S. Baccaro, M. Carewska, C. Casieri, A. Cemmi, A. Lepore, *Polym. Degrad. Stabil.*, **98**, 2005 (2013).
- ²³ M. L. Nelson, R. T. O'Connor, *J. Appl. Polym. Sci.*, **8**, 1325 (1964).
- ²⁴ Th. Măluțan, "Metode de analiză și caracterizare a celulozelor" (in Romanian – Methods of Cellulose

Analysis and Characterization), “Gh. Asachi” Technical University, Iași, 2002, 115 pp.

²⁵ Th. Măluțan, *Celuloză și Hârtie*, **54**, 34 (2005).

²⁶ P. Garside, P. Wyeth, *Restaurator*, **25**, 249 (2006).

²⁷ R. Bodîrlău, C.-A. Teacă, I. Spiridon, *Int. J. Polym. Anal. Charact.*, **15**, 460 (2010).

²⁸ I. Spiridon, C.-A. Teacă, R. Bodîrlău, *BioResources*, **6**, 400 (2011).

²⁹ J. Siroky, T. A. S. Benians, S. J. Russell, T. Bechtold, J. P. Knox *et al.*, *Carbohydr. Polym.*, **89**, 213 (2012).

³⁰ S. Y. Oh, D. I. Yoo, Y. Shin, H. C. Kim, A. Y. Kim *et al.*, *Carbohydr. Res.*, **340**, 2376 (2005).

³¹ Th. Măluțan, V. I. Popa, “Chimia celulozei” (in Romanian – Cellulose Chemistry), Politehniun, Iași, 2008, 200 pp.

³² O. Mălcome, V. Blașcu, J. Homutescu, “Fibre textile” (in Romanian – Textile Fibres), “Gh. Zane” Academic Foundation, Iași, 2000, p. 119.

³³ Carmen-Mihaela Popescu, Iuliana Spiridon, Carmen Mihaela Tibirna and Cornelia Vasile, *J. Photochem. Photobiol. A: Chemistry*, **217**(1), 207 (2011)

³⁴ Qingming Li, Yile Jiang, Xiaojun Su, Xingyao Xiong, Xinghe Tan, Songwen Yu and Qiulong Hu, *Cellulose Chem. Technol.*, **49** (4-5), 423 (2015)