ACADEMIA ROMÂNĂ
Revue Roumaine de Chimie
http://web.icf.ro/rrch/

Rev. Roum. Chim.,
2019, *64*(5), 453-460
Doi: 10.33224/rrch.2019.64.5.09

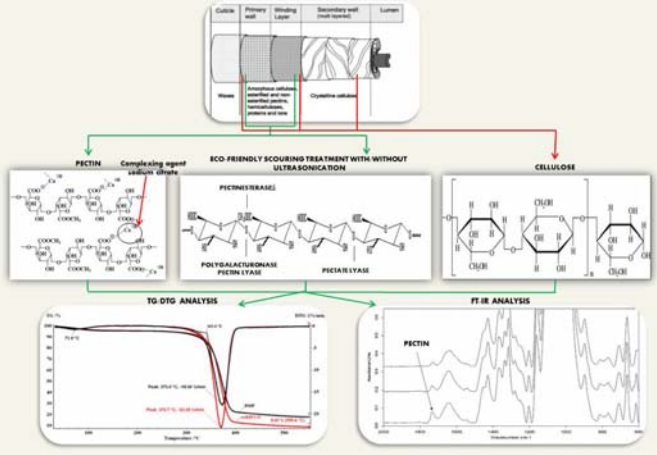
TG/DTG ANALYSIS OF AN ECO-FRIENDLY SCOURED FABRIC

Dorina CHAMBRE,[a] Mihaela DOCHIA[b,*] and Simona GAVRILAŞ[a]

[a]AUREL VLAICU University, Faculty of Food Engineering, Tourism and Environmental Protection, Elena Drăgoi 2-4, 310330 Arad, Roumania
[b]AUREL VLAICU University, Research Development Innovation in Natural and Technical Sciences Institute, Elena Drăgoi 2-4, 310330 Arad, Roumania

Received January 22, 2019

The TG/DTG analysis of the raw cotton-flax fabric (40% flax-60% cotton), bioscoured samples with/without ultrasonication (in the presence of different enzyme concentration and action time) and of the alkaline treated sample has been achieved aiming to study the influence of the experimental conditions on the pectin elimination and quantifying the efficiency of the eco-friendly process. TG/DTG results were correlated with FT-IR data. Even at a short action enzyme time the results demonstrate the efficacy of the ultrasonication in the eco-friendly scouring process, which becomes more pronounced as the enzyme concentration and action time increases.



INTRODUCTION

Cotton – a cellulosic fibre, and flax – a lignocellulosic fibre, are important raw materials for the textile industry due to their qualities like softness, comfortability, durability, freshness and biodegradability.[1-3] Both fibres have a multilayered structure mainly consisting from cellulose (cotton – 86–96%, flax – 70–75%), but also a number of other non-cellulosic components, considered impurities such as pectin (cotton – 0.7–1.2%, flax – 10–15%), waxes, hemicelluloses (flax – 15%), proteins, organic acids, minerals / ashes, etc. that are present in the cuticle and in the primary wall.[4-7] In the present, the textile industry uses these natural fibres both individually and in mixture to obtain a wide range of fabrics. The non-cellulosic content is responsible for the non-wetting behaviour of fibres, causing a number of technical problems during the dyeing and other finishing processes.[2,8,9] For obtaining high quality cellulosic/ lignocellulosic fabrics with sufficient whiteness and wettability, it is necessary to remove the non-cellulosic compounds, especially pectin.[3] Pectin is present in fibres as methyl ester or calcium salts form of the (1-4) poly-D-galacturonic acid and builds a network with its structure that plays a bonding role between cuticle and primary wall.[10] The other impurities are dispersed through the backbone and side chains of pectin.[7,11] The removal of the non-cellulosic constituents from cellulosic/lignocellulosic fibres is called the scouring

* Corresponding author: dochiamihaela@yahoo.com

treatment.[2,3] This is performed in an alkaline way which uses a large quantity of chemicals (NaOH), various chemicals auxiliaries and water at high temperature for pectin degradation by hydrolysis or in biochemically way (bioscouring) by treating the textile materials with an enzyme like pectinases or with a mixture of enzymes in the presence of an polydentate ligands (EDTA) as complexing agent.[12-18] The trend in the textile industry was to replace the alkaline scouring, which is a pollutant method, with eco-friendly scouring treatments that use enzymes. Moreover, lately, the tendency is to replace EDTA, known to be toxic with a biodegradable complexing agent like sodium citrate.[2,7,16,19] In addition, the acceleration of mass transfer during enzyme treatment can be done by ultrasonication.[3]

Although the thermogravimetrical analysis is a widely used technique to study the thermal degradation of cellulosic materials[20-25] so far, it has been used less as an alternative method to common ones (whiteness degree, wettability, FT-IR, etc.) to evaluate the efficiency of the bioscouring treatment. The remanent pectin from the material can be considered an indicator for process efficiency and the study of its influence on the thermal decomposition of cellulose becomes necessary.

Continuing the previous work,[2,12,16,18] in this paper we present the results obtained from TG/DTG analysis in order to study the influence of the experimental conditions (ultrasonication, concentrations and action time of enzyme) on the pectin elimination and to evaluate the efficiency of the bioscouring process of a cotton-flax fabric (40% flax-60% cotton). Efficacy of pectin elimination was estimated from the mass-loss values ($\%\Delta m_2$) recorded for the main decomposition step of cellulose (260–400°C) and from the % residual-mass (at 550°C) values. Also, the FT-IR spectra of the samples were recorded and the effect of the experimental conditions on scouring efficiency was estimated through noticing the changes on the specific bands of the residual pectin located at 2916 cm^{-1}, 2852 $cm^{-1}$and 1731 cm^{-1}.

EXPERIMENTAL

For FT-IR and TG/DTG the following samples were analysed: **raw woven cotton-flax fabric** denoted as **RWF** sample (60% cotton + 40 % flax untreated woven blended fabric without sizing agent, preliminary washed and conditioned); **alkaline treated cotton – flax fabric** denoted as **ATF** sample (raw sample treated at 95 °C with 10 $g.L^{-1}$ sodium hydroxide for 55 minutes); **bioscoured cotton – flax fabric samples** with or without ultrasonication denoted as **usBSFx-y** or **BSFx-y**, respectively (were **x** is the concentration of enzyme, % over weight fiber - o.w.f, and **y** - minutes of the enzyme action time) – **usBSF1-35, usBSF2-15, usBSF2-35, usBSF2-55, usBSF3-35 and BSF1-35, BSF2-15, BSF2-35, BSF2-55, BSF3-35**. The preparation of the samples was done according to the methods presented in a previous work.[26]

The FT-IR and TG/DTG experiments were performed on samples taken from different areas of conditioned cotton-flax fabric (up to 105 °C on Sartorius MA 100 system), chopped and mechanical homogenized. The FT-IR spectra of all investigated samples were acquired using the Bruker Vertex 70 spectrophotometer equipped with the ATR cell, on the 600-3000cm^{-1} wavelength range with a resolution of 4cm^{-1} and 100 scans. The spectra were processed using the OPUS software. The recorded FT-IR spectra were normalized and baseline corrected. The TG/DTG experiments for the investigated cotton fabric samples were performed on a STA 409C Luxx system, produced by Netzsch-Germany. The experiments were conducted on 30-550°C temperature range, at 10 $K{\cdot}min^{-1}$ heating rates, using platinum crucibles in dynamic nitrogen atmosphere (50 $mL.min^{-1}$). The samples mass was ~ 10 mg. The curves were processed using the Netzsch Proteus software. All experiments were done in triplicate.

RESULTS AND DISCUSSION

FT-IR analysis

The FT-IR attenuated total reflectance (ATR) spectroscopy has proven to be useful in the evaluation of the bioscouring process of the cellulosic/lignocellulosic fabrics because can highlight changes in the main non-cellulosic compounds by characterizing the carboxyl acids and esters bands that are present in pectin which do not exist in the cellulose structure.[5,7,27-30] In the FT-IR spectra of the investigated samples shown in Fig.1 the band at 3000cm^{-1}–3600cm^{-1} can be assign to the free OH stretching vibration and to the intra- and intermolecular hydrogen bond related to chemical structure of cellulose.[3,5,9,28] The two bands located at 2917 cm^{-1} and 2851 cm^{-1}, are attributed to the stretching vibration of -CH_2- and -CH- groups from pectin, hemicellulose and waxes.[5,28,29] The bands at around 1731 cm^{-1} and 1642 cm^{-1} are characteristic for pectin and can be assigned to the COOH and $COOCH_3$ groups of polygalacturonic acid and to symmetrical/ asymmetrical oscillations of ionized carboxyl groups -$COO^{(-)}$.[5,15,19,28] It should be noted that the characterization of the carboxyl ion band around 1550 cm^{-1}–1650 cm^{-1} by FT-IR is quite difficult because the OH bending of absorbed water (1642 cm^{-1}) was also observed in this regions[5,30] so, many authors recommend the investigation of the band from 1731 cm^{-1}.[5,15,30] In the 600 cm^{-1}–1500 cm^{-1} - fingerprint area, specific and common bands appear, assigned to cellulose.[19,27,28]

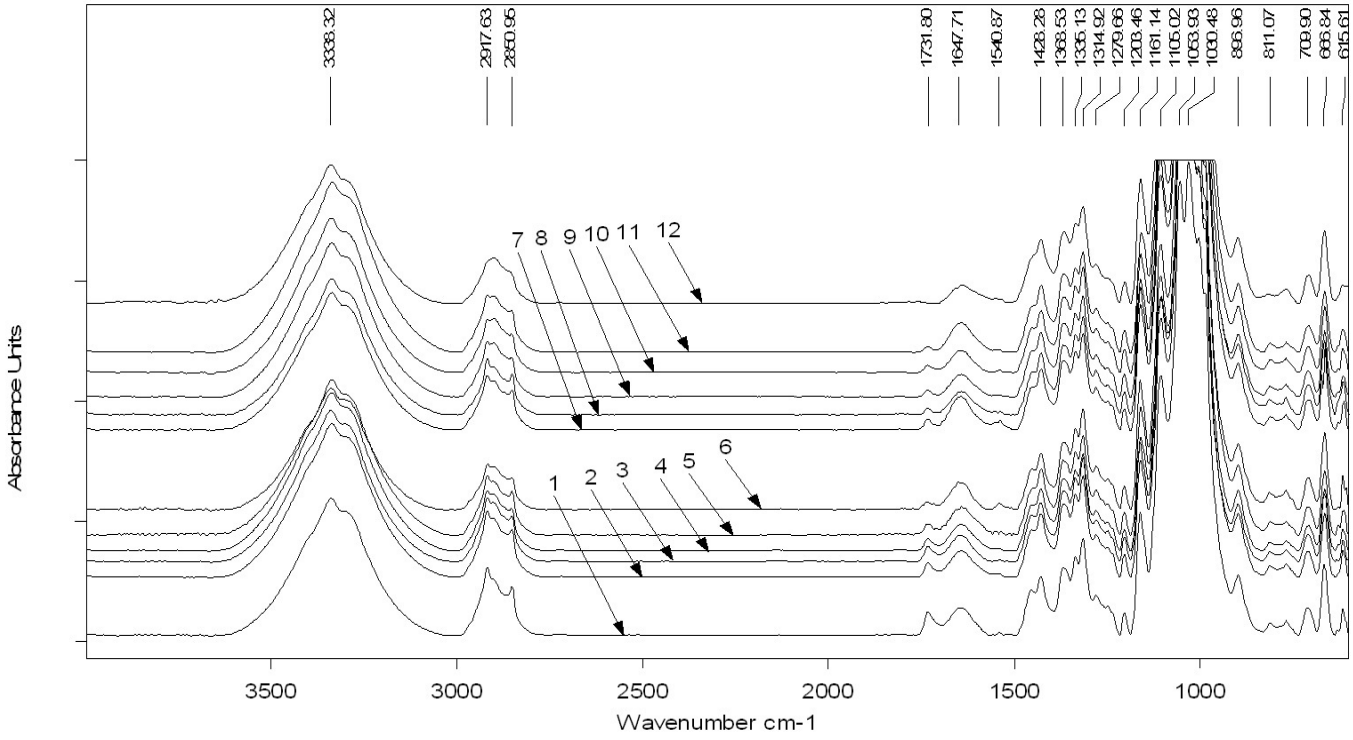


Fig. 1 – FTIR spectra of: 1-**RWF**; 2-**BSF2-15**; 3-**BSF1-35**; 4-**BSF2-35**; 5-**BSF3-35**; 6-**BSF2-55**; 7-**usBSF2-15;** 8-**usBSF1-35;** 9- **usBSF2-35;** 10-**usBSF3-35;** 11-**usBSF2-55;** 12- **ATF**.

Table 1

The relative absorbance values (A_{1731}) of the pectin COOH and $COOCH_3$ groups for the cotton-flax fabric samples

Samples	$A_{1731/\text{ a.u.}}$
RWF	0.465
BSF2-15/ usBSF2-15	0.412/0.229
BSF1-35/usBSF1-35	0.372/0.211
BSF2-35/ usBSF2-35	0.271/0.120
BSF3-35/ usBSF3-35	0.197/0.097
ATF	n.d.
BSF2-55/ usBSF2-55	0.164/0.086

The recorded FT-IR spectra show difference between the pectin bands corresponding to **RWF** and to the treated bioscoured and alkaline fabric samples. The intensity of those two bands located at 2917 cm^{-1} and 2851 cm^{-1} decrease with the increasing of the concentration and action time of enzyme even in the absence of ultrasonication and this behaviour becomes more evident for ultrasonicated samples, respectively for the **ATF** sample. Regarding the band at 1731cm^{-1}, the data reported in Table 1 show the decrease of the relative absorbance values (A_{1731}/a.u.), as the pectin is eliminated from the samples. Similar behaviour was reported in the literature by Wang Q. *et al.* for the characterization of bioscoured cotton fabrics using FT-IR ATR spectroscopy.[5]

With the increase of the concentration and enzyme action time the A_{1731} values of **BSFx-y** decreases relative to **RWF**. For **usBSFx-y** samples the obtained results are considerably lower even at a short time (15 min.) of enzymes action. This behaviour demonstrates the efficacy of the ultrasonication in the bioscouring process which, according with reported data,[5,9] improve the diffusion, mass and heat transfer. However, the vibration peak at 1731cm^{-1} attributed to the C=O stretching of methyl ester and carboxylic acid in pectin does not completely disappear for bioscoured samples suggesting that for the cotton-flax fabric the total elimination of the pectin is quite difficult since flax contains pectin not only on the surface of the fibres but also between the elementary fibres. For **ATF** sample the FT-IR

spectrum suggests the total removal of pectin and hemicelluloses by alkalisation. Also, from Fig.1 it was noticed that, with the exception of **ATF** and **usBSF2-55** for the others bioscoured samples, the bands located at 600 cm^{-1}–1500 cm^{-1} (cellulose fingerprint area) don't present important changes, meaning that the enzyme treatment did not considerably affect the cellulose structure and crystallinity. This behaviour can be an advantage of eco-friendly scouring treatment compared to alkaline treatment which due to its aggressivity, especially at high NaOH concentrations and high temperatures, it can affect the cellulose structure with negative consequences on fabrics quality.[31,32] For the **ATF** and **usBSF2-55** samples an increase in the intensity of the 896 cm^{-1} band ("amorphous" absorption band), assigned to -C-O-C- stretching of β-(1-4)-glycosidic linkages and a decrease of the band at 1428cm^{-1} ("crystallinity band"), assigned to a symmetric -CH_2- bending vibration,[31] were noticed compared to the values obtained for the **RWF** ($A_{896,RWF}$ = 0.421, $A_{1428,RWF}$ = 0.362, $A_{896,usBSF2-55}$ = 0.563, $A_{1428,\ usBSF2-55}$ = 0.302, $A_{896,ATF}$ = 0.679, $A_{1428,\ ATF}$ = 0.209 u.a.). These results suggest a destruction of the crystalline cellulose structure in the presence of alkaline conditions or for a long sonication time. The bands at 1540 cm^{-1} and 811cm^{-1} are specific for lignin from flax component and were diminished in the **ATF** case.

Thermal analysis

The TG/DTG curves recorded in nitrogen atmosphere on 30–550°C for **RWF**, **ATF**, **BSFx-y** and **usBSFx-y** are shown in Fig. 2, Fig. 3 and Fig. 4.

The analysis of the TG/DTG curves shows that the non-isothermal degradation of the investigated cotton-flax fabric samples occurs through two processes accompanied by mass-losses (%Δm). The first process, (%Δm_1), recorded between 60–120°C with the peak temperature on DTG curve at T_{DTG}~72°C is due to the humidity elimination from textile samples. From 120°C to 260°C the samples were quite stable. The second decomposition process corresponds to the main mass-loss stage, (%Δm_2), and was recorded in the 260–400°C temperature range.

In all investigated fabric samples a % residual-mass at 550°C was noticed due to the formation of the carbonaceous residues from polymeric compounds degradation and to the ashes, naturally present in cotton and flax fibres.

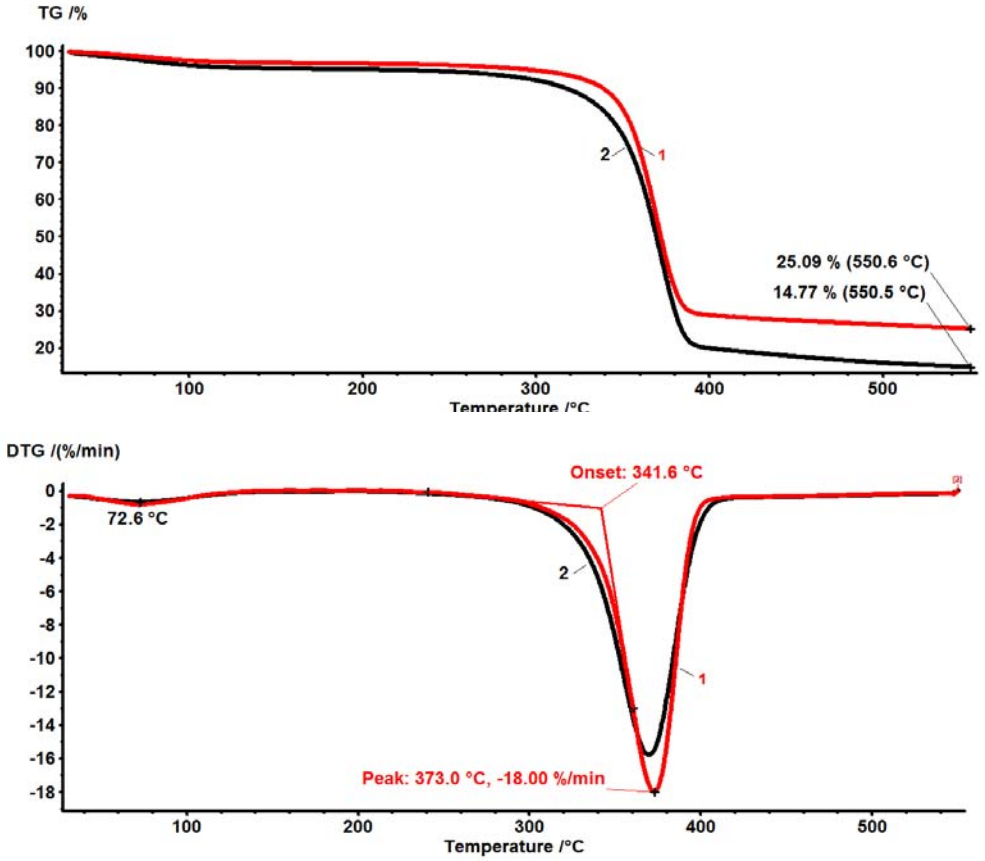


Fig. 2 – TG/DTG curves of 1-**RWF** and 2- **ATF** samples.

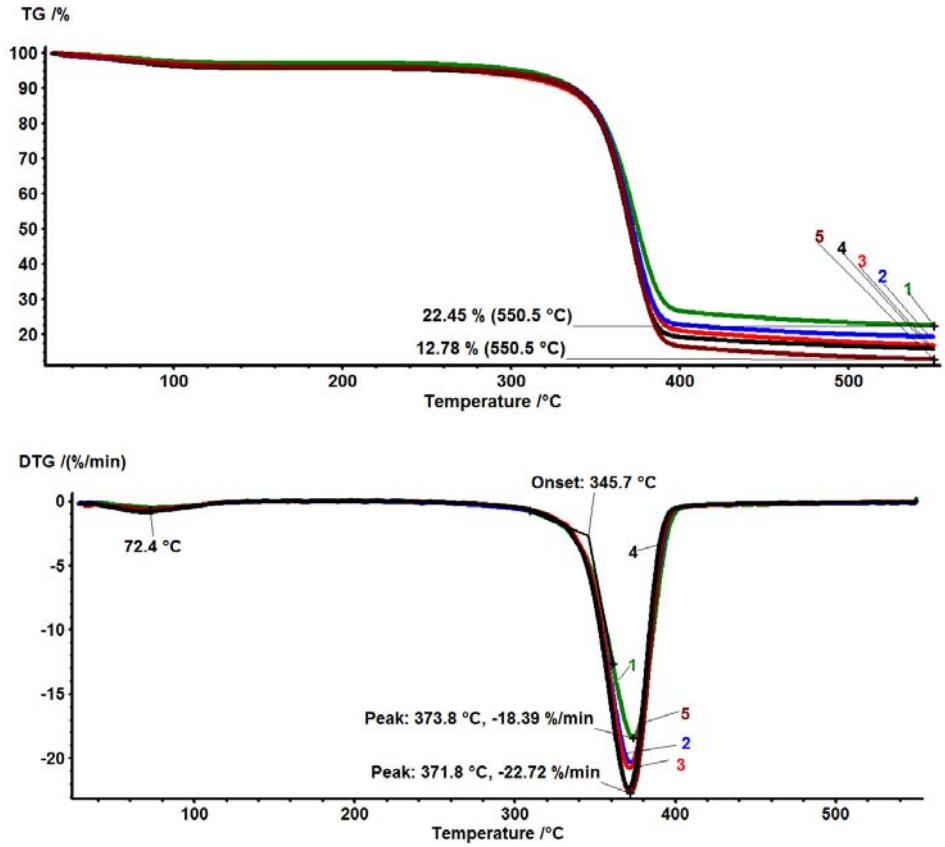


Fig. 3 – TG/DTG curves of: 1-**BSF2-15**, 2-**BSF1-35**, 3-**BSF2-35**, 4-**BSF3-35, 5-BSF2-55** samples.

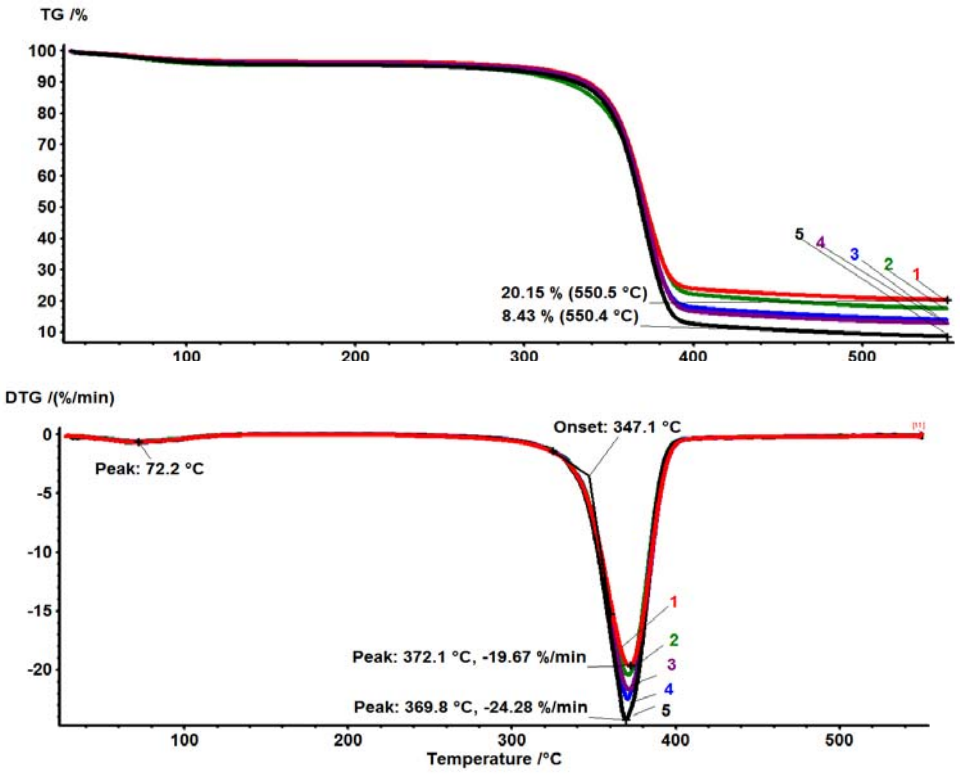


Fig. 4 – TG/DTG curves of: 1-us**BSF2-15**, 2-us**BSF1-35**, 3-us**BSF2-35**, 4-us**BSF2-55, 5-BSF3-35** samples.

Table 2

The main DTG temperature values and -(dΔm/dt) at 370°C for the investigated samples*

Sample	Without ultrasound			With ultrasound		
	T_{onset} /(°C)	T_{DTG} /(°C)	$-(d\Delta m/dt)_{370\,^0C}$ /(%/min)	T_{onset} /(°C)	T_{DTG} /(°C)	$-(d\Delta m/dt)_{370\,^\circ C}$ /(%/min)
RWF	341.6	373.0	17.60	-	-	-
BSF2-15/ usBSF2-15	345.0	373.8	17.61	347.1	372.1	19.45
BSF1-35/ usBSF1-35	345.6	372.3	20.05	347.3	371.3	20.37
BSF2-35/ usBSF2-35	345.7	371.5	20.63	347.8	371.8	21.51
BSF3-35/ usBSF3-35	346.0	371.1	22.23	348.8	369.8	24.26
BSF2-55/ usBSF2-55	346.4	371.8	22.46	346.2	370.8	22.39
ATF	335.3	370.0	15.80	-	-	-

At the beginning of second mass-loss stage, the thermal degradation/pyrolysis of non-cellulosic components structure (especially pectin and hemicelluloses) take place which overlap and influence the cellulose decomposition/pyrolysis reactions.[20] The lignin has been shown to degrade in wide temperature interval (200–550°C)[21] and due to the fact that the bio-treatment with pectinase does not affect the lignin content from the fabric, its influence on the thermal decomposition of the samples is not taken into consideration in this work. It is well known from literature that cellulose has a complex gradual degradation which involves two types of reactions: depolymerisation reaction with formation of levoglucosan that at higher temperature breaks-down to given low molecular-mass volatile compounds (ketones, aldehydes, furans and pyrans) and dehydration reaction with char formation.[20-24] The presence of pectin and small amounts of metallic ions, like calcium pectate from network structure that bonds cuticle and primary wall, could influence the char quantity produced in cellulose degradation.[20]

Consequently, the efficacy of the bioscouring can be estimated from the recorded values of mass-loss ($\%\Delta m_2$) and % residual-mass (at 550°C), these thermal parameters being in correlation with the remaining non-cellulosic and metallic ions content of the cotton-flax fabric samples.

The temperature values where the main decomposition step begins (T_{onset}), obtained from DTG curves, the maximum DTG peak temperature (T_{DTG}) and the values of the derivative for T = 370°C ($(d\Delta m/dt)_{370°C}$) are given in Table 2.

The T_{onset} value obtained from DTG curve for **RWF** is ~342°C being close to the reported value in literature for cotton fabric (T_{DTG} ~347°C).[26] The T_{onset} value slightly increases for bioscoured samples ($T_{onset\ BSCx\text{-}y}$ ~ 345°C, $T_{onset\ usBSCx\text{-}y}$ ~ 347°C) with the removal of non-cellulosic attendants from the fabric.

A more significant variation was observed in the height of the DTG peaks as can be seen from the Fig. 2, Fig. 3 and Fig. 4. The maximum of the DTG peaks (T_{DTG}) corresponds to the inflection point from the TG curves and the values of the derivative indicating the maximum decomposition rate. The T_{DTG} values decrease with ~ 4°C from RWF to BSCx-y and usBSCx-y while the maximum mass loss rate increases from 18.00 %/min. to 22.72 %/min. and 24.27 %/min. for BSF3-35/usBSF3-35. This variation is due to the enzymatic elimination of pectin from the samples, in accordance with the FT-IR results and also to Ca^{2+} ions elimination under the action of the complexing agent.

For a better evaluation of bioscouring efficacy the -(dΔm/dt) values were determined at a fixed temperature (370°C) for all samples. As expected based on FT-IR results, all bioscoured samples presented higher values comparing with RWF sample and the maximum values were obtained for usBSFx-y samples than for the BSFx-y. It should be noted that the -(dΔm/dt) value of the usBSF2-55 sample is lower than that for usBSF3-35 even though the FT-IR results show that for a longer enzyme action time and sonication the pectin elimination was more advanced.

The mass-loss values (%Δm) for the recorded decomposition steps and % residual - mass from the TG curves are presented in Table 3.

Table 3

The % mass-loss and % residual- mass values from the TG curves of the investigated samples*

Sample	Without ultrasound			With ultrasound		
	(%Δm_1) (80-120°C)	(%Δm_2) (260-400°C)	% residual-mass (550°C)	(%Δm_1) (80-120°C)	(%Δm_2) (260-400°C)	% residual-mass (550°C)
RWF	3.03±1.12	68.15±1.13	25.09±0.16	-	-	-
BSF2-15/ usBSF2-15	3.04±1.48	69.25±0.81	23.45±1.05	4.86±1.12	73.27±1.35	20.15±1.12
BSF1-35/ usBSF1-35	4.27±1.14	73.67±0.43	19.19±0.98	4.81±1.77	76.09±0.90	17.42±0.88
BSF2-35/ usBSF2-35	3.57±1.32	76.83±0.54	15.67±0.81	4.48±1.42	78.32±0.97	13.89±1.87
BSF3-35/ usBSF3-35	4.53±0.64	77.07±0.89	15.06±0.65	4.52±0.98	83.31±1.22	8.43±1.65
BSF2-55/ usBSF2-55	4.74±1.22	78.86±1.44	12.78±1.12	4.04±1.16	78.94±0.87	13.71±1.42
ATF	4.10±1.11	76.40±0.55	14.77±0.88	-	-	-

* Values are the average of three determinations

It can be seen that all samples have approximately the same humidity (%Δm_1 = 3.03 – 4.86%). In the case of **RWF** sample, the lowest value for the %Δm_2 and the highest value for % residual-mass at 550°C were recorded. This behaviour is due to the high content of non-cellulosic components (pectin, hemicelluloses and waxes) which decompose at lower temperatures (~337.9°C) than cellulose. A higher content of pectin lead to a higher amount of char formation. The char could limit the rate of cellulose decomposition by delaying the volatility rate of the gases produced.[32] Hence, the removal of pectin from the surface of cotton and flax fibres in bioscouring treatment caused a greater rate of cellulose mass loss (see Table 2) and led to the increasing of %Δm_2 and to diminishing of % residual-mass. For **BSFx-y** samples the increase of the enzyme concentration in the treatment bath from 1% o.w.f. to 2% o.w.f. determined the increase of %Δm_2 values with ~3% and the decrease in % residual-mass by ~4%. A subsequent increase in enzyme concentration to 3% o.w.f. did not significantly affect the mass-loss values. Similarly, the increase of enzyme action time from 15 min. to 35 min. led to a larger amount of pectin removal than the increase from 35 min. to 55 min. These results are in good agreement with the previously obtained data related to the influence of the bioscouring conditions on the hydrophilic properties of the cotton fabric.[16] Compared to the **BSFx-y** samples, the **usBSFx-y** showed, for the same enzyme conditions, higher values for %Δm_2 and lower values for % residual-mass (550°C), respectively. This demonstrates the efficacy of the ultrasonication for a larger amount of pectin removal even at a short action time of enzyme (15 min.). These results are in line with those obtained from the FT-IR analysis and data from Table 2. In the ultrasonication conditions the powerful agitation of the liquid border layer caused by cavitation substantively improve the transport of bulky enzyme molecules toward the fabric surface and increase the overall reaction rate. For the **ATF** sample, even if the FT-IR results indicate advanced pectin elimination, the thermal stability is lower than for the raw woven fabric and all eco-friendly treated samples ($T_{onsetATF}$ ~335°C). This can be explained by the fact that some of the hydrogen bonds between the cellulose polymers chains were degraded by NaOH, reducing the crystallinity, as it was noticed by the "amorphous" and "crystallinity" bands modifications. Besides, the modification in cellulose molecular chains with the formation of low molecular weight fragments it can occur which accelerate the thermal degradation process. On the other hand, any remaining Na^+ metal ions may be present as (–O Na^+) groups and can depress the degradation rate ($-(d\Delta m/dt)_{370}{}^0{}_C$ = 15.80 %/min.) of cellulosic chains influencing the (%Δm_2) and % residual-mass values. The obtained TG/DTG results for **usBSF2-55** sample can be also explained by changes in the cellulose crystallinity noticed in the intensity bands located at 896 cm^{-1} and 1428 cm^{-1}. By prolonging the time of ultrasonication, a local overheating may appear and affect the structure of the cellulose chains. Thus, a change in the cellulose decomposition mechanism takes place, which alters the decomposition rate ($-(d\Delta m/dt)_{370}{}^0{}_C$ = 22.39 %/min.) and the % mass-loss (%Δm_2=78.94).

CONCLUSIONS

The influence of the ultrasonication and enzyme conditions on the pectin elimination in eco-friendly scouring treatment of a cotton-flax fabric (40% flax-60% cotton) was investigated by FT-IR and TG/DTG thermal analysis and the obtained results were in a good agreement (except the **usBSF2-55** sample). The data showed an increasing of T_{onset} of the main decomposition step for the bioscoured samples compared to row fabric due to the non-cellulosic components elimination. A larger amount of pectin eliminated led to increases of the decomposition rate and mass loss values in the main degradation stage of cellulose and to the diminishing of % residual-mass. The presence of metallic ions can depress the thermal degradation of cellulosic chains affecting the degradation rate (-(dΔm/dt), mass-loss (%Δm_2) and % residual-mass values. The influence of the ultrasonication on pectin elimination can be observed even at a short action time of enzyme (15 min.) on the textile substrate, but a prolonged treatment can destroy the macromolecular and crystallinity structure of the cellulose chains, altering the values of TG/DTG thermal parameters. By correlating with other specific analyses, the TG/DTG can be used for quantifying the efficiency of the fabrics bioscouring process.

Acknowledgements. This work was supported by a grant of the Roumanian National Authority for Scientific Research and Innovation, CNCS – UEFISCDI, project number PN-II-RU-TE-2014-4-1370.

REFERENCES

1. P. J. Wakelyn, N. R. Bertoniere, A. D. French, D. P. Thibodeaux, B. A. Triplett, M. A. Rousselle, W. R. Goynes, J. V. Edwards Jr., L. Hunter, D. D. McAlister and G. R. Gamble, "Cotton Fibers", in "Handbook of Fiber Chemistry", 3th edition, Taylor & Francis Group, New York, 2007, p. 523.
2. M. Dochia, M. D. Stanescu and C. Constantin, *Fibres Text. East. Eur.*, **2013**, *21*, 22-25.
3. S. Perincek and K. Duran, *J. Clean. Prod.*, **2016**, *135*, 1179-1188.
4. C. Lin and Y. L. Hsieh, *Text. Res. J.*, **2001**, *71*, 425-434.
5. Q. Wang, X. Fan, W. Gao and J. Chen, *Carbohyd Res.*, **2006**, *341*, 2170-2175.
6. G. R. Gamble, *J. Agr. Food Chem.*, **2003**, *51*, 7995–7998.
7. E. S. Abdel-Halim, H. M. Fahmy and M. G. Fouda Moustafa, *Carbohyd. Polym.*, **2008**, *74*, 707-711.
8. Q. Wang, X. Fan, Z. Hua, W. Gao and J. Chen, *Biocatal. Biotransfor.*, **2007**, *25*, 8-15.
9. C. Vigneswaran, M. Ananthasubramanian and N. Anubumani, *Indian J. Fibre Text.*, **2013**, *38*, 44-56.
10. B. L. Ridley, M. A. O'Neill and D. Mohnen, *Phytochemistry*, **2001**, *57*(6), 929–967.
11. K. Sawada, S. Tokino, M. Ueda and X. Wang, *J. Soc. Dyers Colour.*, **2003**, *114*, 333-336.
12. M. D. Stanescu, M. Fogorasi, S. Mihuta, M. Dochia and V. I. Lozinsky, *Rev. Chim.*, **2009**, *60*, 59-62.
13. M. Calafell and P Garriga, *Enzyme Microb. Technol.*, **2004**, *34*, 326-331.
14. R. Araujo, M. Casal and A. Cavaco-Paolo, *Biocatal. Biotransfor.*, **2008**, *26*, 332-349.
15. C. Chung, M. Lee and E. K. Choe, *Carbohyd. Polym.*, **2004**, *58*, 417-420.
16. M. D. Stanescu, M. Dochia, D. Radu and C. Sirghie, *Fibres Text. East. Eur.*, **2010**, *18*, 109-11.
17. S. Kalantzi, D. Mamma, P. Christakopoulos and D. Kekos, *Bioresour. Technol.*, **2008**, *99*, 8185-8192.
18. M. D. Stanescu, M. Fogorasi, M. S. Bucur, M. Pustianu and M. Dochia, *Sci. Bull. B Chem. Mater. Sci. UPB*, **2010**, *72*, 21-28.
19. S Alix, E. Philippe, A. Bessadok, L. Lebrun, C. Morvan and S. Marais, *Bioresour. Technol.*, **2009**, *100*, 4724-4729.
20. I. Cabrales and N. Abidi, *J. Therm. Anal. Calorim.*, **2010**, *102*, 485-491.
21. E. Corradini, E. M. Teixeira, P. D. Paladin, J. A. Agnelli, O.R.R.F. Silva and L. H. C., *J. Therm. Anal. Calorim.*, **2009**, *97*, 415-419.
22. A. L. F. S. d'Almeida, D. W. Barreto, V. Calado and J. R. M. d'Almeida, *J. Therm. Anal. Calorim.*, **2008**, *91*, 405-408.
23. A. A. Saafan and A. M. Habib, *J. Therm. Anal. Calorim.*, **1987**, *32*, 1511-1519.
24. C. M. Tian, Z. H. Shi, H. Y. Zhang, J. Z. Xu, J. R. Shi and H. Z. Guo, *J. Therm. Anal. Calorim.*, **1999**, *55*, 93-98.
25. L. Zhang, J. He and S. Y. Wanh, *J. Therm. Anal. Calorim.*, **2009**, *2*, 653-659.
26. M. Dochia, D. Chambre, S. Gavrilas and C. Moisa, *J. Therm. Anal. Calorim.*, **2018**, *132*, 1489-1498.
27. L.Bílková, *Polym. Degrad. Stab.*, **2012**, *97*, 35-39.
28. Z. Kovačević, S. Bischof Vukušić and M. Zimniewska, *Text. Res. J.*, **2012**, *82*, 1786-1798.
29. K. Subramanian, P. Senthil Kumar, P. Jeyapal and N. Venkatesh, *Eur. Polym. J.*, **2005**, *41*, 853-861.
30. J. Čopiková, A. Synytsya, M. Černá, J. Kaasová and M. Novotá, *Czech J. Food Sci*, **2001**, *19*, 51-56.
31. D. Ciolacu, F. Ciolacu and V. I. Popa, *Cellul. Chem. Technol.*, **2011**, *45*, 13-21.
32. S. Ouajai and R. A. Shanks, *Polym. Degrad. Stab.,* **2005**, *89*, 327-335.