ON THE THERMAL STABILITY OF FLAX FABRICS GRAFTED WITH MONOCHLOROTRIAZINYL-β-CYCLODEXTRIN AND TREATED WITH CINNAMIC DERIVATIVES

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Cyclodextrins are among the most frequently used host molecules in inclusion compounds chemistry, with a wide applicability in different fields, including the textile industry.
The thermal stability over the 25-900 °C temperature range of several flax samples grafted with monochlorotriazinyl-β-cyclodextrin and treated with cinnamic derivatives (ferulic acid, caffeic acid, ethyl ferulate) has been studied. The influence of the heating rate and atmosphere (air and nitrogen) under which the thermal degradation of the investigated samples occurred was also underlined.
The thermal methods (TGA, DSC) applied to the flax grafted with MCT-β-CD and treated with different cinnamic derivatives have evidenced a complex mechanism of thermal degradation.
The degradation mechanisms of the investigated flax samples are similar, consisting of two stages: in the former, the physically bonded water is removed (approximately 4%) while, in the latter, the mass loss is of about 75-80%.

Keywords: monochlorotriazinyl-β-cyclodextrin, cinnamic derivatives, flax grafting, thermal analysis

INTRODUCTION

Cyclodextrins are cyclic, non-reducing oligosaccharides, built up from 6 to 12 α-1,4-linked D(+)-glucopyranose units. Due to their specific molecular structure, presenting hydrophobic nanocavities, the main characteristic of cyclodextrins is their ability to form inclusion compounds with a great variety of guest molecules. Cyclodextrins (CD) are among the most frequently used host molecules in supramolecular chemistry, having a wide applicability in different fields, including textile industry.[1-10]

Thermogravimetrical analysis allows to estimate the kinetic parameters of thermal degradation (reaction rate constant, k, reaction order, n, and activation energy, E_a). The values of these parameters are especially significant for elucidating the mechanisms of the degradation reaction and for estimating the thermal stability of the chemical compounds.[11-13]

Differential microcalorimetry records the thermal effects (exo- and endothermic) accompanying the modification in sample structure and/or microstructure. Otherwise said, the variation of the sample temperature may be caused by the caloric effects (exo- and endothermic) that appear after the physical transitions or after the chemical reactions developed in the sample during heating or cooling. In the case of differential microcalorimetry, the sample, as well as the reference material, are maintained under

isothermal conditions by applying a differential electric energy. The amount of additional energy (as electric power dQ/dt) necessary to maintain the sample under the same temperature conditions as those of the reference material is recorded as a function of either time or temperature.

When heated, the polymer sample absorbs a certain amount of energy and passes into a plastic state, because of the mobility of its macromolecular chains, the process being endothermic. The crystallization of the amorphous regions of a polymer is accompanied by an energy release and, therefore, the process is exothermic. When the polymer reaches the melting point, it absorbs energy and the macromolecular chains become more mobile and more disordered. All these changes (*e.g*. phase transitions, melting, crystallization, vaporization, dissociation, decomposition and oxido-reduction reactions, etc.) may be recorded on a thermogram using differential calorimetry.

Considering all these aspects, the thermal stability within the 25-900 °C temperature range of several flax samples grafted with monochlorotriazinyl-β-cyclodextrin and treated with cinnamic derivatives has been studied. The flax fabrics grafted with monochlorotriazinyl-β-cyclodextrin and treated with cinnamic derivatives have been previously evaluated by elemental analysis, UV and FT-IR-transmission.[3,4]

EXPERIMENTAL

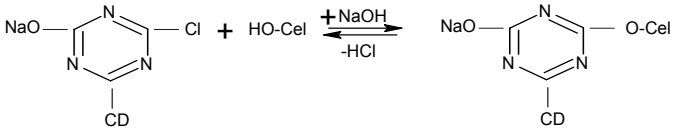
Materials

Monochlorotriazinyl-β-CD (MCT-β-CD or CAVATEX W7 MCT, Wacker Chemie, Germany) was grafted on a cellulosic support (a 100% flax fabric with a yarn fineness of 50/2 tex, cloth binding and specific mass of 211 g/m^2).

Three guest substances have been used: ferulic acid (*trans*) [3-(4-hydroxy-3-methoxyphenyl)-2-propenoic acid] (FA) (Fluka AG), caffeic acid (3,4 dihydroxy-cinnamic acid) (CA) (Merck) and ethyl ferulate (EF) (synthetized in the laboratory).

Methods

The grafting of MCT-β-CD on the cellulosic support takes place according to reaction (1):



(1)

The impregnation of the conditioned flax fabric in an alkaline solution of CAVATEX W7 MCT (5 min), under magnetic stirring, was followed by the squeezing and air-drying of the samples. After a 15-min oven-curing at 130 ºC, the samples were thoroughly washed with warm and cold distilled water, to attain a 6.5-7 pH value, and then dried at room temperature. The grafted material was used as a support for the inclusion of three guest compounds (FA, CA, EF). The quantities of the guest compound for a grafted sample were calculated for a grafting degree of 5.71% and an inclusion ratio of 1:1. The samples were immersed for 22 h in the guest compound solution (with a concentration of 10 g/L in a 7/3 ethylic alcohol/water mixture), for the formation of the inclusion compound. The excess reagents were removed by four successive warm and cold washings with distilled water, followed by cold extraction in an ethylic alcohol/water mixture (7/1), at a bath ratio of 1:40. Finally, the flax samples were dried at room temperature and conditioned.

Analyses

Thermal analysis was performed on a Mettler Toledo TGA-SDTA 851e derivatograph, under nitrogen atmosphere, at a 20 mL/min flow rate, at a heating rate of 10-15 ºC/min (within the 25-900 ºC temperature range; sample mass: 3.1-4.7 mg). To obtain comparable data, the operational parameters were kept constant. The kinetic interpretation was realized with the STARe soft offered by Mettler Toledo. To ensure data reproducibility, several thermograms have been recorded for each sample.

Differential calorimetry (DSC) data were registered on a differential calorimeter Mettler DSC 12E (Switzerland), using 87-95 mg fabric samples. The samples were conditioned for 72 h in a dessicator with salt solutions up to a humidity level of 65%. The heating rate was of 10 °C/min. The calibration in the caloric effect of the device was performed before each set of measurements, using indium.

RESULTS AND DISCUSSION

Differential thermal analysis

After analysing the TG curves recorded at a heating rate of 15 ºC/min, under inert atmosphere, the thermogravimetric characteristics presented in Table 1 have been obtained.

The degradation mechanisms of the flax samples investigated are similar, consisting of two stages: in the former, the physically bonded water is removed (approximately 4%) while, in the latter, the mass loss is of about 75-80%.

The effects of the heating rate on the position and shape of the TG curves (explained by the fact that the modification of this parameter influences the processes of mass and heat transfer) were investigated by recording the TG curves at a heating rate of 10 ºC/min, the other operational parameters being held constant. The thermogravimetric characteristics obtained are presented in Table 2 and the DTG curves are shown comparatively at 10 and 15 ºC/min, respectively (Figs. 1-5). A shift in the temperature of the peaks to values lower with approximately 4-10 ºC, at a heating rate of 10 ºC/min, is observed.

Table 1
Thermogravimetric characteristics (15 ºC/min, in nitrogen)

Sample	Stage	T_{onset}, ºC	T_{peak}, ºC	T_{endset}, ºC	W %	Residue, %
Ungrafted flax	I	50	69	113	4.08	16.82
	II	313	368	388	79.10	
Flax grafted with MCT-β-CD	I	50	79	121	2.45	18.04
	II	318	363	385	79.51	
Flax grafted with MCT-β-CD and treated with FA	I	50	101	104	4.02	13.61
	II	183	189	205	3.46	
	III	320	376	387	78.91	
Flax grafted with MCT-β-CD and treated with CA	I	50	65	105	4.57	18.13
	II	150	196	220	0.9	
	III	317	372	388	76.4	
Flax grafted with MCT-β-CD and treated with EF	I	50	73	108	3.97	18.2
	II	300	371	387	77.83	

T_{onset} – the temperature at which the thermal degradation begins in each stage; T_{peak} – the temperature at which the degradation rate is maximum in each stage; T_{endset} – the temperature at which the thermal degradation ends in each stage; W % – the percentage mass loss in each stage; Residue – the amount of degraded sample remaining at temperatures higher than 900 °C

Table 2
Thermogravimetric characteristics (10 ºC/min, in nitrogen)

Sample	Stage	T_{onset}, ºC	T_{peak}, ºC	T_{endset}, ºC	W %	Residue, %
Ungrafted flax	I	45	54	99	3.52	18.08
	II	267	362	379	78.40	
Flax grafted with MCT-β-CD	I	52	68	117	6.14	18.04
	II	306	359	377	80.36	
Flax grafted with MCT-	I	45	59	115	3.91	16.18

β-CD and treated with FA	II	165	185	196	2.24	
	III	302	366	380	77.67	
Flax grafted with MCT-β-CD and treated with CA	I	47	64	115	4.63	16.76
	II	293	362	380	78.61	
Flax grafted with MCT-β-CD and treated with EF	I	49	59	91	3.76	17.54
	II	291	365	379	78.70	

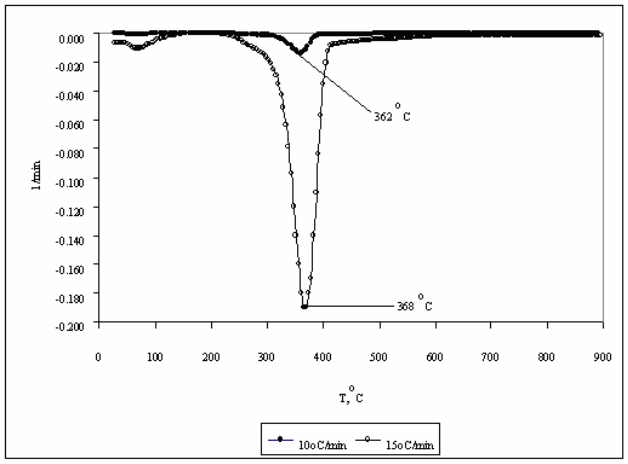


Figure 1: DTG curves for ungrafted flax at two heating rates

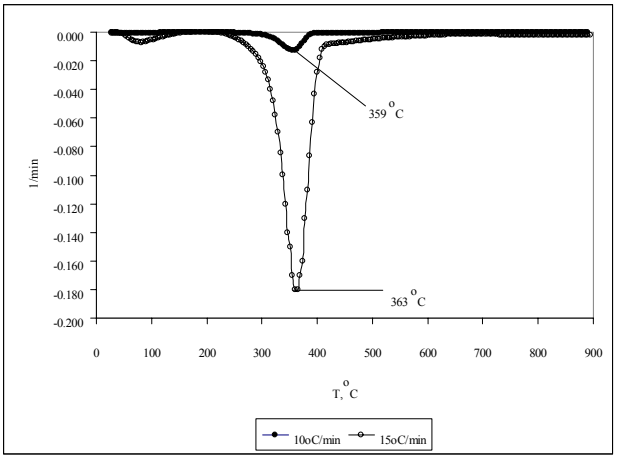


Figure 2: DTG curves for flax grafted with MCT-β-CD at two heating rates

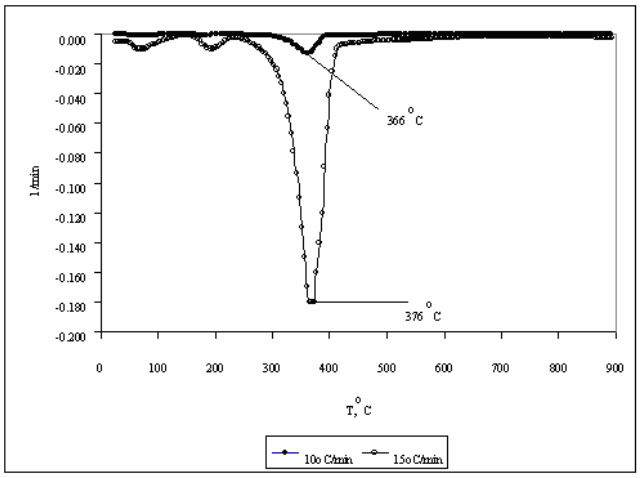


Figure 3: DTG curves for flax grafted with MCT-β-CD and treated with FA at two heating rates

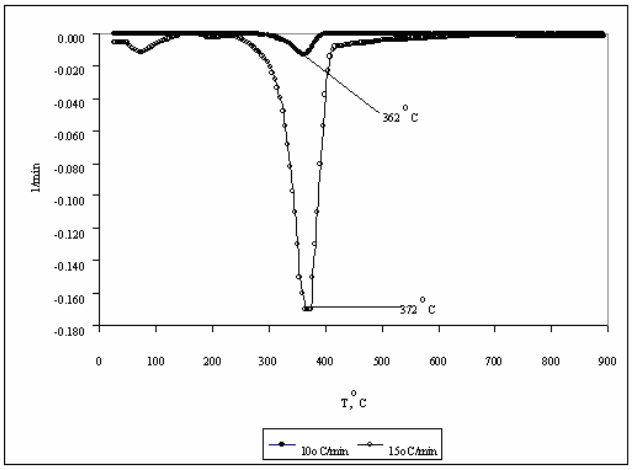


Figure 4: DTG curves for flax grafted with MCT-β-CD and treated with CA at two heating rates

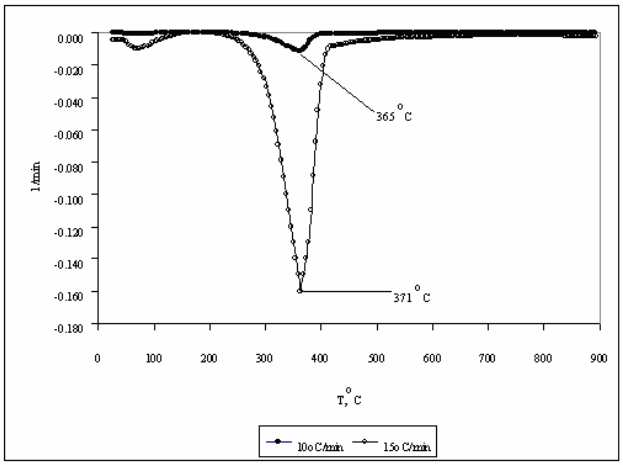


Figure 5: DTG curves for flax grafted with MCT-β-CD and treated with EF, at two heating rates

To establish the influence of the medium in which the sample is placed during heating, the thermograms have been recorded for flax samples grafted with MCT-β-CD and treated with cinnamic derivatives, both in air and nitrogen, at the same rate of 10 ºC/min. The TG curves obtained are plotted in Figs. 6-10. The thermogravimetric characteristics for the curves recorded in air at 10 ºC/min are presented in Table 3. On analyzing the results, one can conclude that the atmosphere under which degradation occurs influences the process of the thermal decomposition. Thermal degradation in air takes place in three stages, with different mass loss percentages. Thus, the presence of the air favours the degradation while, in inert gas, the degradation is reduced, as demonstrated by the higher quantity of residues remaining when working under nitrogen.

The last stage of thermal degradation, occurring at temperatures over 350 ºC, is represented by the thermooxidation of the carbonic residue.

The studies have been extended to the kinetic processing of the thermo-gravimetric data. The application of the Freemann-Caroll method, based on the equation

$$\frac{\Delta \ln \frac{d\alpha}{dT}}{\Delta \ln(1-\alpha)} = n - \frac{Ea}{R} \times \frac{\Delta\left(\frac{1}{T}\right)}{\Delta \ln(1-\alpha)} \quad (1)$$

led to the kinetic characteristics presented in Tables 4 and 5.

By plotting $\Delta\ln(d\alpha/dT)/\Delta\ln(1-\alpha)$ *versus* $\Delta(1/T)/\Delta\ln(1-\alpha)$, the activation energy E_a may be calculated from the slope of the straight line and the reaction order n – from the origin intercept. The pre-exponential factor is determined with the following equation:

$$\frac{d\alpha}{dT} = \frac{1}{a} A \exp(\frac{-Ea}{RT}) f(\alpha) \quad (2)$$

The close values of the activation energies and of the reaction orders determined at the two heating rates confirm that the degradation mechanisms for flax fabrics grafted with MCT-β-CD and treated with cinnamic derivatives are similar.

Table 3
Thermogravimetric characteristics (10 ºC/min, in air)

Sample	Stage	T_{onset}, ºC	T_{peak}, ºC	T_{endset}, ºC	W %	Residue, %
Ungrafted flax	I	67	80	115	7.25	
	II	289	348	371	55.57	2.77
	III	371	487	547	34.41	
Flax grafted with MCT-β-CD	I	56	101	130	7.5	1.89
	II	301	355	361	54.78	

	III	361	471	543	35.83	
Flax grafted with MCT-β-CD and treated with FA	I	56	84	110	6.72	0.87
	II	110	165	300	7.87	
	III	300	348	351	47.86	
	IV	351	466	520	36.68	
Flax grafted with MCT-β-CD and treated with CA	I	60	104	141	7.76	3.42
	II	141	222	324	7.45	
	III	324	359	371	44.09	
	IV	371	491	547	37.28	
Flax grafted with MCT-β-CD and treated with EF	I	57	85	119	6.75	3.5
	II	278	363	372	54.87	
	III	372	479	581	34.88	

Table 4
Values of the kinetic parameters for the second stage of thermal degradation (15 ºC/min) under nitrogen atmosphere

Sample	E_a (kJ/mol)	n	ln A	r^2
Ungrafted flax	182.45	0.61	29.59	0.98
Flax grafted with MCT-β-CD	167.93	0.85	27.16	0.99
Flax grafted with MCT-β-CD and treated with FA	146.61	0.51	22.55	0.99
Flax grafted with MCT-β-CD and treated with CA	154.9	0.68	24.29	0.97
Flax grafted with MCT-β-CD and treated with EF	100.96	0.48	13.92	0.98

A – pre-exponential factor; E_a – apparent activation energy; n – reaction order; r^2 – correlation coefficients

Table 5
Values of the kinetic parameters for the second stage of thermal degradation (10 ºC /min) under nitrogen atmosphere

Sample	E_a (kJ/mol)	n	ln A	r^2
Ungrafted flax	171.61	0.85	27.61	0.97
Flax grafted with MCT-β-CD	173.92	1.12	28.34	0.98
Flax grafted with MCT-β-CD and treated with FA	152.20	0.65	23.65	0.99
Flax grafted with MCT-β-CD and treated with CA	151.09	0.75	23.56	0.98
Flax grafted with MCT-β-CD and treated with EF	96.74	0.43	12.85	0.98

A – pre-exponential factor; E_a – apparent activation energy; n – reaction order; r^2 – correlation coefficients

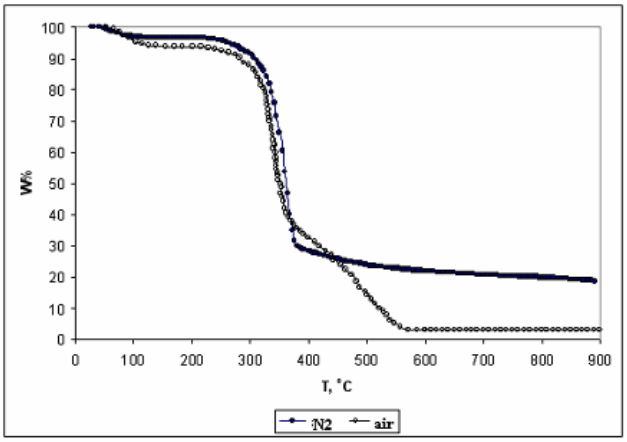


Figure 6: TG curves for ungrafted flax, at a heating rate of 10 ºC/min, in air and nitrogen

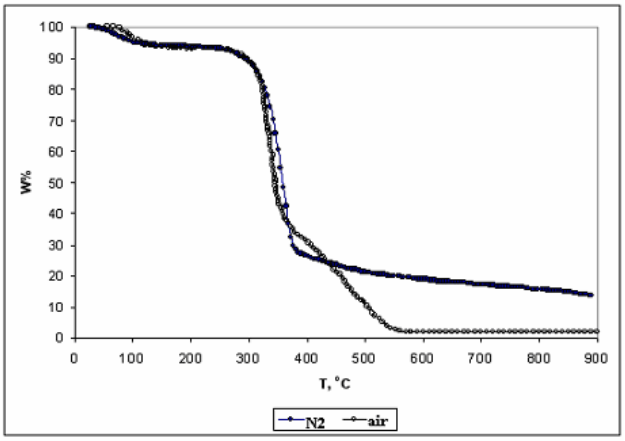


Figure 7: TG curves for flax grafted with MCT-β-CD at a heating rate of 10 ºC/min, in air and nitrogen

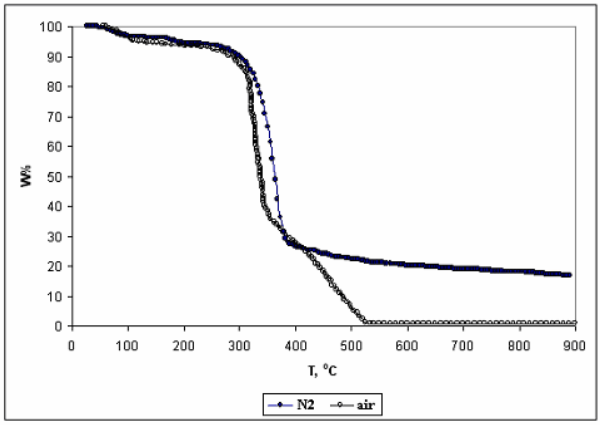


Figure 8: TG curves for flax grafted with MCT-β-CD and treated with FA at a heating rate of 10 ºC/min, in air and nitrogen

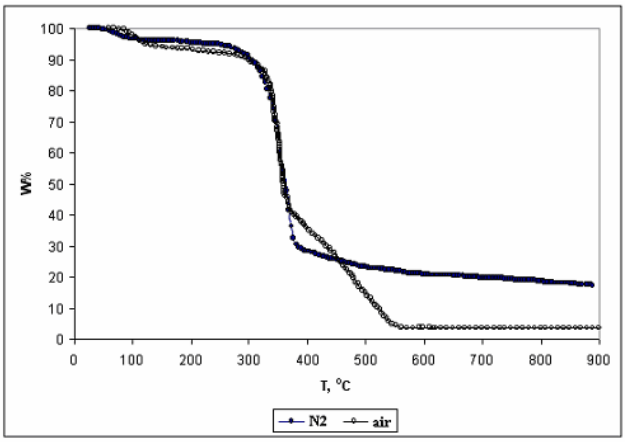


Figure 9: TG curves for flax grafted with MCT-β-CD and treated with CA at a heating rate of 10 ºC/min, in air and nitrogen

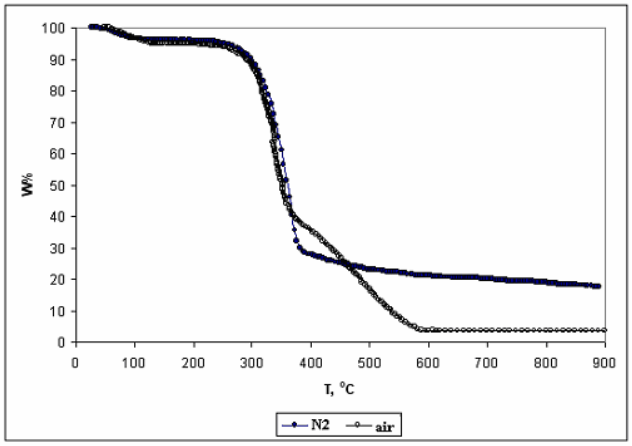


Figure 10: TG curves for flax grafted with MCT-β-CD and treated with EF at a heating rate of 10 ºC/min, in air and nitrogen

Differential microcalorimetry (DSC)

The recording of the thermograms was performed in two stages: in the former, the heating of the samples led to water elimination (20-150 °C) while, in the latter, the sample was destroyed (50-350 °C).

The analysis of the DSC thermogram recorded for an inclusion compound of CD offers information on its purity. The DSC curves for all above-mentioned inclusion compounds indicate the absence of the endothermic peaks corresponding to non-included guests. Due to CDs decomposition during heating, it is not possible to trace the presence of free CD by DSC analysis.

The major advantage of the DSC method consists in the fact that the area of the thermogram peaks is directly proportional to the variation in the enthalpy of the samples, therefore it can be applied to measure the thermal capacity, the heat of fusion and the reaction enthalpies. The enthalpy of evaporation (Table 6) was calculated with the equation

$$\Delta H = \frac{S_x}{E \cdot m_x} \quad (3)$$

where ΔH = enthalpy of evaporation (J/g); E = 4.02 μV/mW (sensitivity of the calorimeter); S = peak area (mm^2), estimated gravimetrically; S_x = S x k; S_x = peak area corrected with a correction factor k (μV); m_x = mass of the dried sample (mg).

The slight increase in the enthalpy (the increase in hydrophilicity) might be partially explained by the splitting of the hydrogen bonds in the cellulose structure and by the grafting of MCT-β-CD to the hydroxyl groups. After the inclusion, a part of the hydroxyl groups are involved in host-guest interactions, which explains the decrease in hydrophilicity for the samples treated with cinnamic derivatives.

Table 6
Values of the evaporation enthalpy for untreated and treated flax samples

No.	Sample	Enthalpy of evaporation ΔH, J/g
1	Ungrafted flax	23.156
2	Flax grafted with MCT-β-CD	29.873
3	Flax grafted with MCT-β-CD and treated with FA	24.087
4	Flax grafted with MCT-β-CD and treated with CA	27.070
5	Flax grafted with MCT-β-CD and treated with EF	24.779

CONCLUSIONS

- The thermal methods (TGA, DSC) applied to the flax grafted with MCT-β-CD and treated with different cinnamic derivatives (ferulic and caffeic acids, ethyl ferulate) have evidenced a complex mechanism of thermal degradation in which the presence of both host and guests on the cellulose support influences the thermal behaviour. Thus, the thermal stability of the flax grafted with MCT-β-CD and treated with FA and CA, respectively, decreases, while the thermostability of the flax grafted with MCT-β-CD and of that grafted with MCT-β-CD and treated with EF is similar to that of the ungrafted flax.
- The degradation mechanisms of the investigated flax samples are similar, involving two stages: in the former, the physically bonded water is removed (approximately 4%) while, in the latter, the mass loss is of about 75-80%.
- The influence of the heating rate and of the atmosphere under which thermal degradation occurred (air and nitrogen) in the investigated samples was also underlined. The presence of air favours degradation while, in the inert gas, the degradation is reduced, as demonstrated by the higher quantity of residues remaining when working under nitrogen.

- The close values of the activation energies and of the reaction orders determined at the two heating rates (10 and 15 ºC/min) confirm that the degradation mechanisms for flax fabrics grafted with MCT-β-CD and treated with cinnamic derivatives are similar.
- DSC analysis shows a slight increase in the enthalpy (increase in hydrophilicity), which might be partially explained by the splitting of the hydrogen bonds in the cellulose (flax) structure and by the grafting of MCT-β-CD to the hydroxyl groups.

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