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## Chemical modification of hemp shives and their characterization

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### Abstract

Lightweight lignocellulosic composites are potentially contributing to sustainable development. However, lignocellulosic fillers are not always fully compatible with an inorganic matrix, which causes a variety of adverse outcomes such as the coherence and mechanical properties of composites. Therefore, experiments are made with natural fiber surface treatment. Experiments were conducted to further development of natural fibers - hemp shives of another application to lightweight composites. Untreated and chemically treated hemp shives surfaces by NaOH, Ca(OH)<sub>2</sub> and EDTA were characterized by FTIR and TG. Changes in the FTIR spectra at 1730, 1625 and cm<sup>-1</sup> indicated that hemicellulose and lignin from natural fiber surfaces were removed by alkaline treatment. Thermal stability of hemp shives was studied using thermal gravimetric and DSC method.

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*Keywords:* Renewable source; hemp; chemical treatment; modification; analytical evaluation; FTIR; TG

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### 1. Introduction

One of the possible ways of achievement of sustainable development in the building industry is moving from the limited and finite material resources to easily renewable raw material resources. A large group of renewable raw materials are materials of plant origin, of which a great importance is attached to

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technical hemp like an easily renewable source of cellulosic fibers with potential for reinforcement of composite and non-waste material [1]. Renewal of scientific as well as industrial interests in the use of cellulosic fibres and especially hemp fibres as load bearing constituents in lightweight composite materials relates to a need of progress of environmental friendly products with high use value in term of sustainable development. Nowadays, hemp is regarded to be of important industrial and economic value as a source not only of building materials but of paper, textiles, food, medicine, paint, detergent, varnish, oil, ink, and fuel too [2]. The new research field of hemp fibres utilisation is application such as biodiesel production from hempseed oil and textiles production from hemp stems [3].

Due to low density, biodegradability, interesting thermal, mechanical, acoustic and aseptic properties of hemp fibres, low cost and eco-friendly raw material, this natural fibrous material is used as a (partial) replacement of synthetic fibres, such as glass, carbon or metallic fibres. During their growth, harvesting and processing consume overall less fossil energy and chemicals than the synthesis of man-made fibres, their use decreases consequently the carbon dioxide emissions associated with the composite fabrication. [4]. However, one of the major disadvantages of natural fibres is their high moisture sorption sensitivity causing the chemical degradation of the structure of fibres as well as dimensional variations of fibers according to the moisture content and their heterogeneity, which leads to a weak adhesiveness on interface between the fibres and the matrix and to a poor transfer of the applied stress between the materials. This last effect has an impact on the quality of the mechanical interaction between hemp fibres and matrix. The presence of surface impurities and the large amount of hydroxyl groups make plant fibers less attractive for reinforcement of materials too [5, 6].

The surface treatment is necessary in order to optimise the adhesive strength in composites reinforced with natural fibres. The main objective of chemical modification is to remove pectins from the middle lamella in order to separate fibre bundles in fibrils. This fibrillation should lead to an increase the surface area available for chemical bonding between the fibres and the matrix and to appear a more homogeneous surface made of cellulose, which will probably enhance the adhesion between the fibres and the matrix [7].

In this paper, chemical treatment of the surface hemp shives in different environments (NaOH,  $\text{Ca}(\text{OH})_2$ , EDTA-ethylene-diamine-tetra acetic acid at laboratory temperature was performed in order to separate fibre bundles in fibrils and change chemical behaviour or surface state of fibres for their application into lightweight composites. ATR-FTIR and TG were used for identification of changes in the chemical and physico-chemical properties of treated hemp shives in comparison to untreated shives.

## 2. Materials and Methods

Hemp shives used in experiments represent the woody parts of stems of plant - *Cannabis Sativa* that is free from plant fibers. The final fibre length of used technical hemp shives coming from the Netherlands company Hempflax ranged between 4 mm and 0,063 mm. The chemicals which were applied to treatment of fibres, NaOH, Ethylene-diamine-tetracetic acid (EDTA) were all of analytical grade, calcium hydroxide was 96%, pulverized. The characteristics of chemicals are given in Table 1. Chemical modification of hemp shives was performed follow to literature [6]:

Treatment – alkalization: The natural dried hemp shives (vol. humidite up to 10%) were soaked in 1.6 M NaOH solution during 48 h and then neutralized in a 1 vol. % acetic acid. Fibres were then washed with deionised water until the pH value was 7.

Treatment by  $\text{Ca}(\text{OH})_2$ : In order to saturate fibres with calcium ions, fibres were placed in a saturated lime solution ( $[\text{Ca}^{2+}] = 2 \cdot 10^{-2} \text{ M}$ ) for 48 h. After treatment hemp shives were rinsed with deionised water (conductivity 0,02mS) and dried in oven during 48 h at 50°C.

Treatment by EDTA: Fibres were immersed during 3 h in a solution of EDTA (5 g/l). In order to ensure removal of excess EDTA, fibres were then washed with deionised water and dried oven during 48 h at 50°C.

Table 1. Chemicals used for modification of hemp shives surface

Chemicals	Formula / purity	Producer
calcium hydroxide	Ca(OH) <sub>2</sub> ≥96%, pulv	ROTH, Germany
sodium hydroxide	NaOH p.a.	CHEMAPOL, Slovakia
ethylene-diamine-tetracetic acid	C <sub>10</sub> H <sub>16</sub> O <sub>8</sub> N <sub>2</sub> , p.a.	GAVAX s. r. o., Slovakia
acetic acid	CH <sub>3</sub> COOH; 8vol.%	GAVAX s. r. o., Slovakia

Both methods Fourier transform infrared spectroscopy (FTIR) with ATR unit and thermal analysis (TG/DSC) were used for identification of changes in the chemical properties of chemically treated hemp shives in comparison to untreated shives. Alpha Bucker Platinum - ATR spectrometer was used to identify the natural and modified hemp shives by measuring the transmitted radiation in a spectral range of 4000–360 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>. A total of 24 scans were taken for each measuring sample.

TG/DSC analysis of hemp shives carried out by using equipment STA 449F3 (Netzsch, Germany). The thermal decomposition of samples was conducted with a heating rate of 10 K/min, from 25 to 1000°C, under nitrogen atmosphere, using the DSC/TG pan, material corundum-Al<sub>2</sub>O<sub>3</sub>.

### 3. Results and discussion

#### 3.1. FTIR evaluations

FTIR spectra of hemp shives treated by three reagents are compared with untreated sample in Fig. 1. Table 2 summarizes the major bands observed in the spectra of hemp shives and their assignments to chemical group vibrations and molecules. The peak at 3340 cm<sup>-1</sup> is characteristic for stretching vibration of the hydrogen bonded hydroxyl group (OH) in polysaccharides. The characteristic stretching vibration of CH observed at 2919 cm<sup>-1</sup> belongs to group in cellulose and hemicelluloses [14]. The peak at 2897 cm<sup>-1</sup> was attributed to C–H stretching vibrations of all hydrocarbon constituents present in the fibres and the shoulder band observed at 1731±2 cm<sup>-1</sup> was due to the carbonyl (C=O) stretching vibration of the acetyl groups of hemicellulose present in the hemp shives. The peak appearing at 1454 cm<sup>-1</sup> was attributed CH<sub>2</sub> bending vibrations in lignin and the peak at 1319 cm<sup>-1</sup> corresponding to OH in-plane bending. A small sharp band at 896 cm<sup>-1</sup> appears to have arisen from β-glycosidic linkages between the sugar units in hemicellulose and cellulose. The next small band at 664 cm<sup>-1</sup> corresponds to COOH bending polysaccharides. Preliminary results of chemical modifications of hemp shives by FTIR spectroscopy confirmed the changes of hemp shives associated with removing of impurities as well as pectin, hemicelluloses, lignin and waxes [15]. The characteristic vibrations of function groups at 2919 and 1734 cm<sup>-1</sup> viewable in spectrum of original hemp shives was disappeared in modified hemp shives what confirmed some chemical changes due to their alkalization. The absence of the peak about 1734 cm<sup>-1</sup> is in good accordance to literature data [8, 9]. This fact is illustrated in Fig. 1 and in detailed form in Fig. 2.

Table 2. Vibration of function groups present in hemp shives

Wavenumber (cm <sup>-1</sup> )	Vibration of function groups	Source
3340	OH stretching	polysaccharides
2919	CH stretching	cellulose, hemicellulose
2897	C–H symmetrical stretching	polysaccharides
1731	C=O unconjugated stretching acetyl groups	hemicellulose
1632	OH (water)	water
1625	C-H symmetrical stretching	cellulose
1504	C=C aromatic symmetrical stretching	lignin
1454	C=C aromatic symmetrical stretching	lignin
1319	O–H in-plane bending	cellulose
1029	C-C, C-OH, C-H ring and side group vibration	hemicellulose, pectin
896	β-glycosidic bonds symmetrical ring-stretching mode	polysaccharides
664	COOH bending peaks	polysaccharides

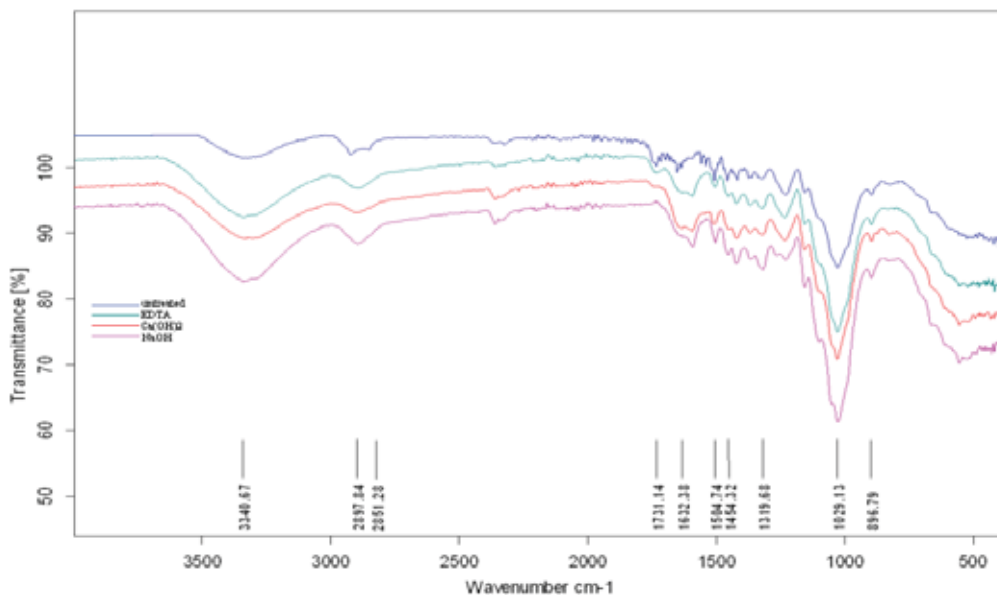


Fig. 1. Comparison of FTIR spectra of the untreated and treated hemp shives by Ca(OH)<sub>2</sub>, EDTA, NaOH

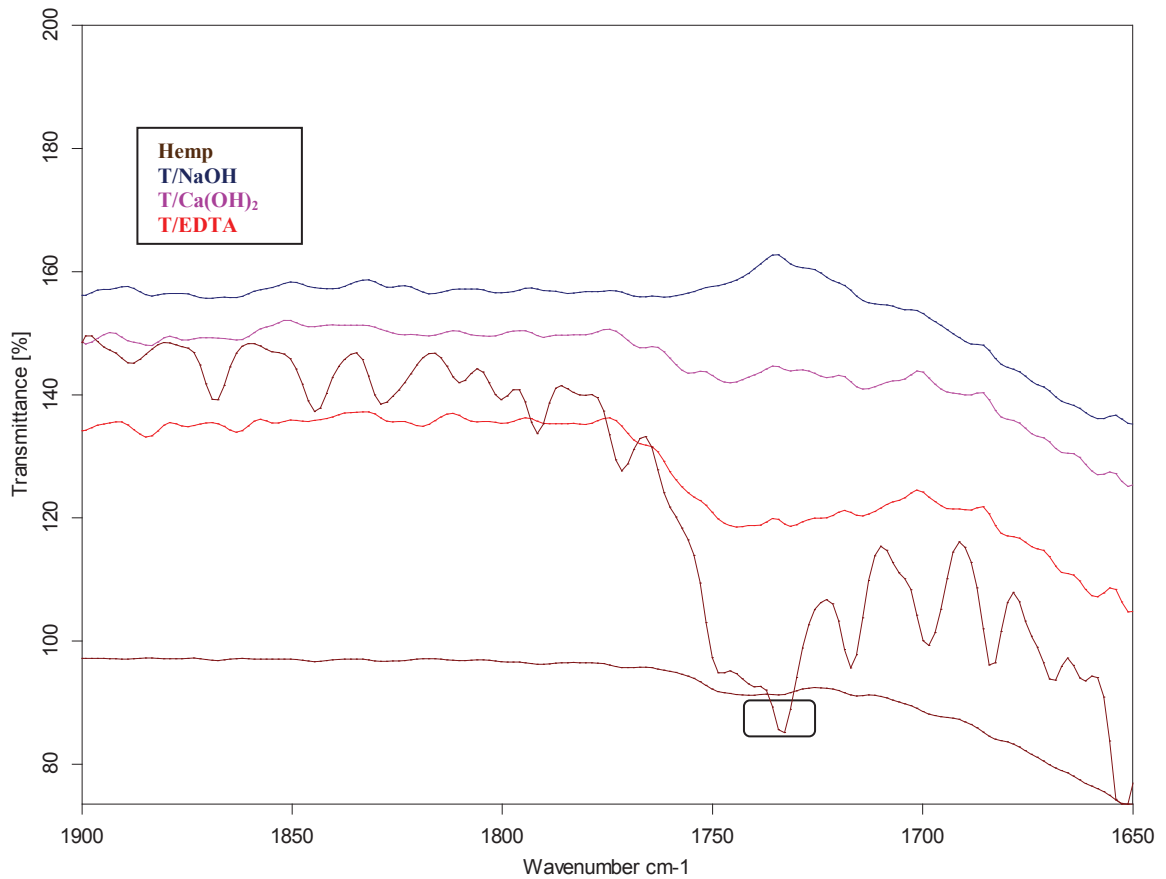


Fig. 2. Details of peak changes at  $1734\text{ cm}^{-1}$  due to chemical treatment of hemp shives (T- treatment)

Some changes observed at vibration peaks  $1507\text{ cm}^{-1}$  and  $1454\text{ cm}^{-1}$  in spectra (Fig. 3) appear due to lignin removing after chemical treatment (absence of C=C aromatic symmetrical stretching vibrations of lignin).

The comparison of FTIR spectra in the range of  $890\text{--}900\text{ cm}^{-1}$  (Fig. 4) shows the partial shift in vibration peaks of shives samples after chemical treatments. This fact confirms probably starting the defibrillation of shives [9, 10, 13].

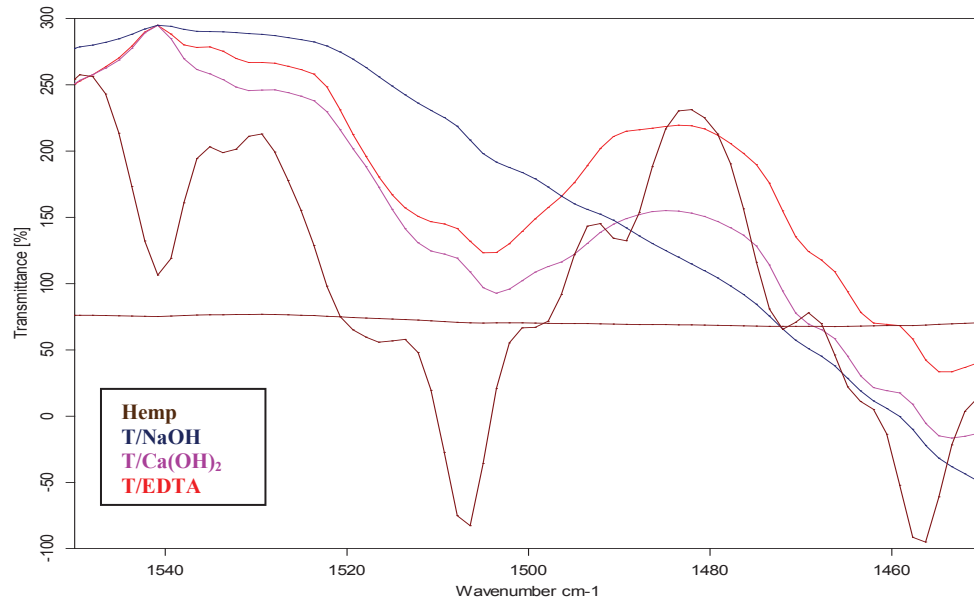


Fig. 3. Changes in FTIR spectra of initial and chemically treated of hemp shives in range of 1400-1550 cm<sup>-1</sup>

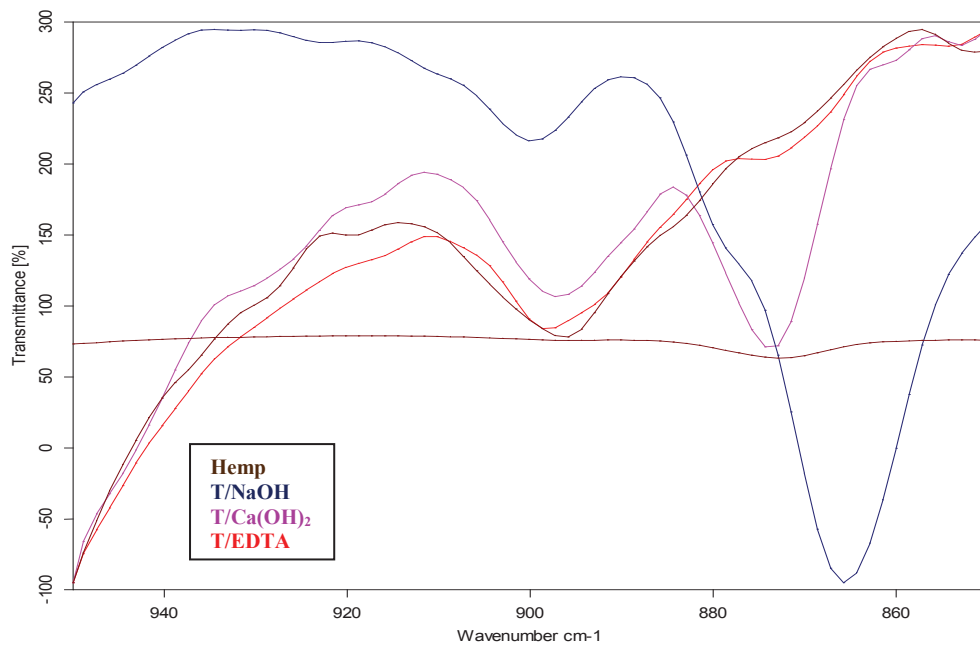


Fig. 4. Comparison of FTIR spectra of initial and chemically treated of hemp shives in range 950- 850cm<sup>-1</sup>

### 3.2. Thermal behavior of hemp shives before and after treatment

For purpose verification of whole thermal stability untreated hemp shives, thermal analysis in the wide range of temperatures up to 1000°C was realized. As it is shown in Fig. 5, thermal decomposition beginning approximately at 190°C and finished at 350°C with top at 280°C. Mass loss was 56.49 wt. % due to thermal decomposition of cellulose and lignin.

The thermogravimetry (TG) curve of untreated hemp shives show an initial peak between 50 and 108°C, which corresponds to a mass loss of absorbed moisture of approximately 4.46 wt.%. After this peak, the TG curve showed three decomposition steps:

- (1) the first decomposition shoulder peak at about 250-335°C is attributed to thermal depolymerisation of hemicelluloses or pectin (mass loss of 24.67 wt.%);
- (2) the major second decomposition peak at about 358-381°C is attributed to cellulose decomposition (mass loss of wt.17.8%);
- (3) the small peak at 381.0-389.8 °C (mass loss of 1.4 wt.%) may be attributed to oxidative degradation of the charred residue in accordance with literature [9,11].

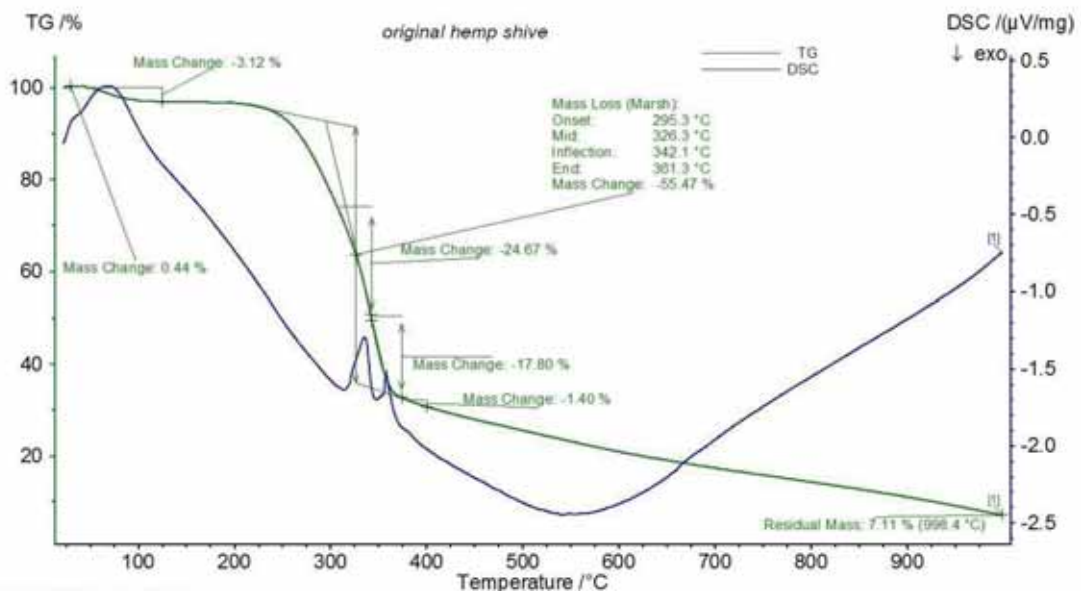


Fig. 5. Thermal analysis of original hemp shives

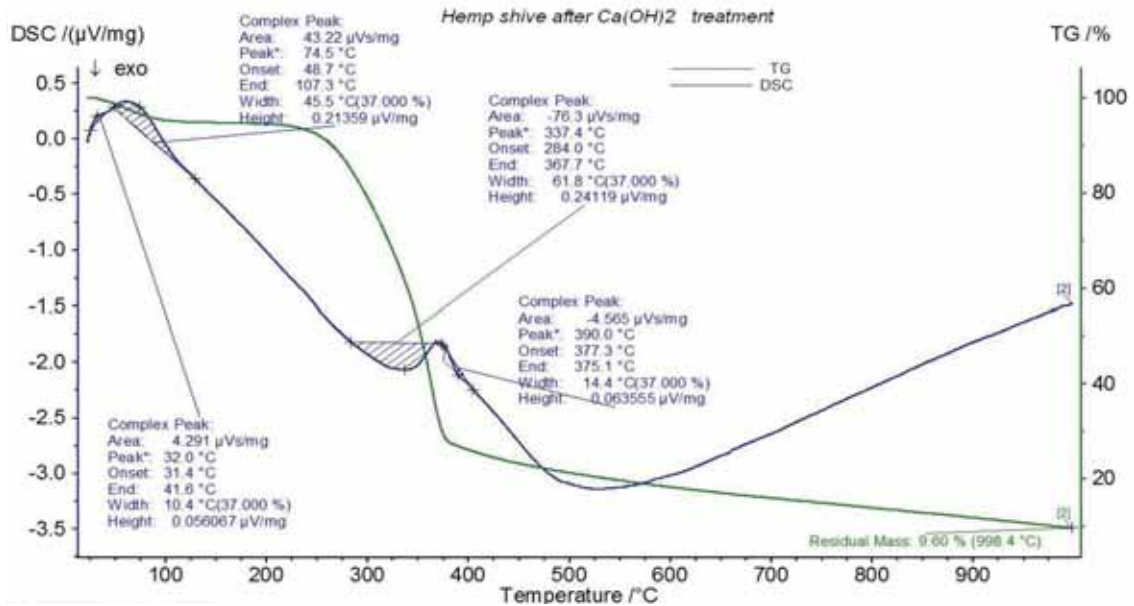


Fig. 6. Thermal analysis of hemp shives after Ca(OH)<sub>2</sub> treatment

The TG/DSC curves of hemp shives after Ca(OH)<sub>2</sub> treatment (Fig. 6) present mass loss of 1.33 wt.% in range 31.4–41.6°C and mass loss of 3.99 wt.% in range 48.7–107.3 °C due to a mass loss of absorbed moisture. The TG curve showed only 2 decomposition steps:

- (1) the first decomposition shoulder peak at about 284–368°C (top of peak–337.4°C) is attributed to thermal depolymerisation of hemicelluloses or pectin (mass loss 55.70 wt%);
- (2) the second decomposition peak at about 377– 399°C is attributed to cellulose decomposition (mass loss 3.78%).

The TG/DSC curves of hemp shives after NaOH treatment (Fig. 7) present mass loss of 0.01 wt.% in range 32.3–42.3°C and mass loss of 2.78 wt.% in range 78.4–115.8 °C due to a mass loss of adsorbed moisture. After this mass loss, the TG curve shows the next decomposition steps:

- (1) the decomposition of sample with top peak at 371.9°C (onset - 369°C end decomposition about 410°C) is represented by mass change of 50.88 wt%;
- (2) the next decomposition of sample with onset on 432.°C peak (top peak 470.3°C) is attributed to cellulose decomposition (mass loss of 4.03wt%);
- (3) the last thermal decomposition process was at temperature of 777.0°C with mass loss of 1.3 wt. %.

The results of TG/DSC of hemp shives treated in NaOH are in accordance with [9,11] and according to authors more non-cellulosic material was removed and the high degree of structural order was retained. However, both non-cellulosic components and the crystalline order of cellulose played an important role in thermal degradation of the fibres.



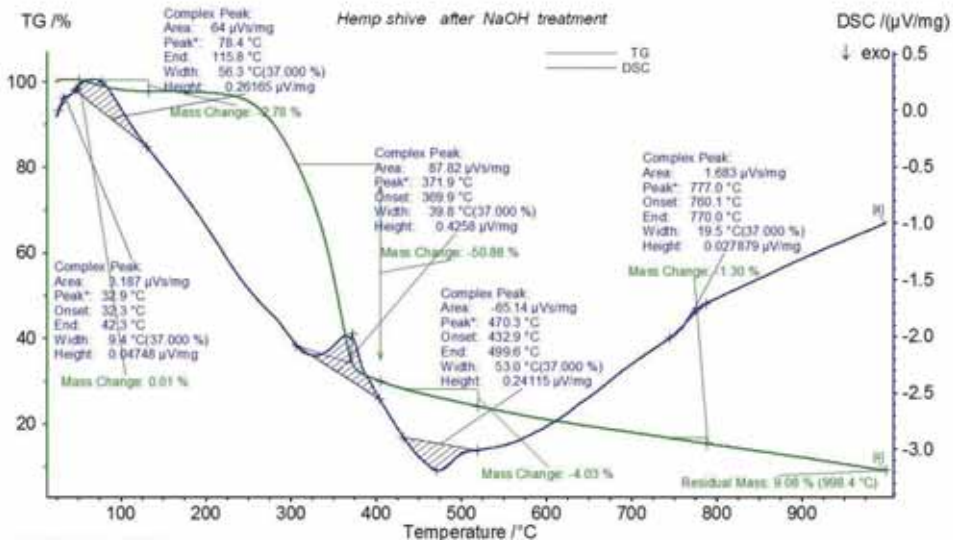


Fig. 7. Thermal analysis of hemp shive after NaOH treatment

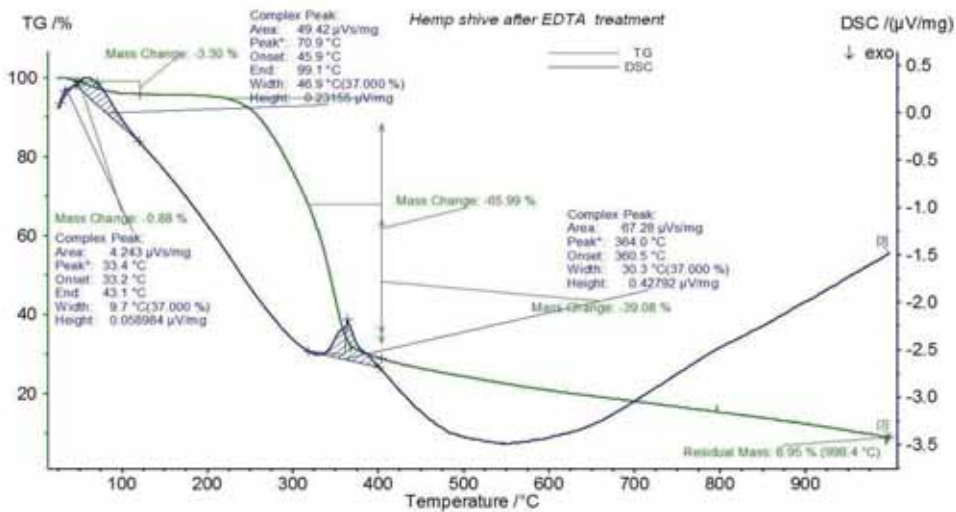


Fig. 8. Thermal analysis of hemp shives after EDTA treatment

The plot of thermal decomposition of hemp shives after EDTA treatment is in Fig. 8. The TG/DSC curves of hemp shives after EDTA treatment present mass loss of 0.88 wt.% in range 33.2-43.1  $^{\circ}\text{C}$  and mass loss of 3.3 wt.% in range 45.9-99.1  $^{\circ}\text{C}$ , (top of peak at 70.9  $^{\circ}\text{C}$ ) due to a adsorbed moisture loss. Follow to evaluation of TG/DSC this sample appears similar pattern of decomposition such as hemp shives after  $\text{Ca}(\text{OH})_2$  treatment then the TG curve showed only 2 decomposition steps: the first mass

change takes place gradually from 105.5-360°C the mass loss is 65.9 wt.%; the next mass loss with onset 365.5°C (top of peak-364.0°C) is attributed to thermal depolymerisation of hemicelluloses or pectin (mass loss 39.08 wt%).

The overall comparison of the appearance of TG curves is summarized in Fig. 9.

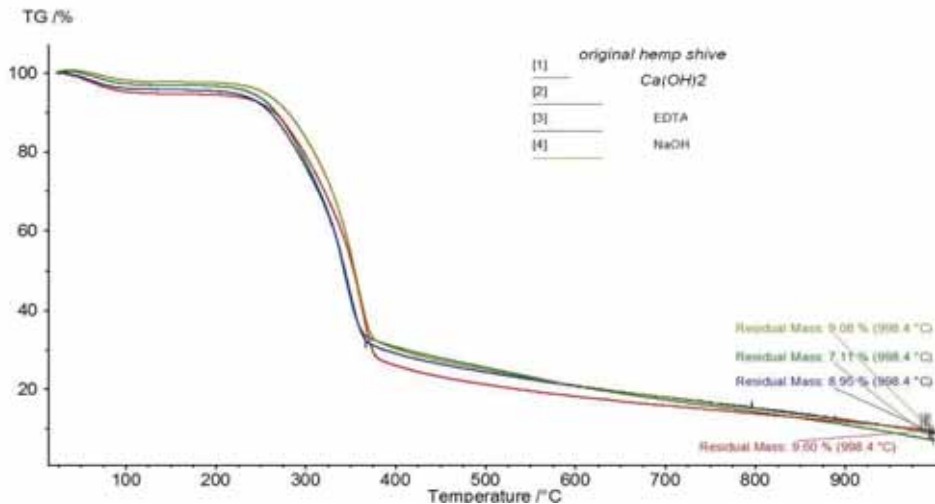


Fig. 9. Comparison of TG curves of hemp shives after all treatments

The total mass losses are in sequence: original hemp shives (residual mass 7,1 wt.%), treated by EDTA (8,95 wt.%), NaOH (9,08 wt.%), Ca(OH)<sub>2</sub> (9,60 wt.%). Thermal stability of hemp shives is an important parameter, since hemp shives is used as filler into composites. In our previous work was therefore investigated the thermal conductivity and resistance of such composites in elevated temperatures [14, 15].

#### 4. Conclusions

The influence of chemical treatment of hemp shives on their properties and thermal stability was studied. Experiments were conducted to characterize the surfaces of treated and untreated fibers and to investigate differences due to chemical modification by using FTIR spectroscopy and TG/DSC analysis.

IR measurements of hemp fibres properties after several chemical treatments indicate that each considered treatment has a direct action onto the fibre surface. Observing the spectra, we found that a partial removal of hemicellulose, lignin and waxes was performed.

Depending on the used chemical agents nature the changes in the surface of hemp shives occur. They are connected with degradation of the amorphous materials present in the fiber structure.

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