Surface Treated Natural Fibres as Filler in Biocomposites

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Abstract. Biocomposites based on natural fibres as organic filler have been studied for several years because traditional building materials such as concrete are increasingly being replaced by advanced composite materials. Natural fibres are a potential replacement of glass fibres in composite materials. Inherent advantages such as low density, biodegradability and comparable specific mechanical properties make natural fibres an attractive option. However, limitations such as poor thermal stability, moisture absorption and poor compatibility with matrix are challenges that need to be resolved. The primary objective of this research was to study the effect of surface treatment on properties of hemp hurds like a natural lignocellulosic material and composites made thereof. Industrial hemp fibre is the one of the most suitable fibres for use in composite materials because of its good specific properties, as well as it being biologically degradable and CO\(_2\) neutral. Improving interfacial bonding between fibres and matrix is an important factor in using hemp fibres as reinforcement in composites. In order to improve interfacial bonding, modifications can be made to the hemp fibres to remove non-cellulosic compounds, separate hemp fibres from their bundles, and modify the fibre surface. This paper contains the comparison of FTIR spectra caused by combination of physical and chemical treatment of hemp material with unmodified sample. Modification of hemp hurds was carried out by NaOH solution and by ultrasonic treatment (deionized water and NaOH solution were used as the cleaning mediums).

1. Introduction

Principles of sustainable construction of the buildings bring new requirements to develop sustainable materials. The use of construction and building materials made from renewable resources is generally regarded as an indispensable option so the construction industry can become more sustainable. The use of wood species in the production of cement composites is particularly interesting for the construction industry. This represents a large opportunity in the field of vegetable fibres that is cost-effective and environmentally friendly. Therefore, promoting the use of cementitious building
materials reinforced with vegetable fibres could be a way to achieve sustainable and more eco-efficient construction [1].

In this respect, there is a large group of materials of plant origin, which are rapidly renewable raw materials that can be used as a suitable reinforcement component to lightweight composites [2]. Traditional building materials are increasingly being replaced by advanced composite materials in accordance with sustainable development requirements. Fiber reinforced polymers and fibre reinforced cement represent this group of new composites with advantageous properties [3]. Lignocellulosic biomass has become a promising alternative source of materials for industrial applications. Cellulose, hemicelluloses and lignin are the major components of biomass. Cellulose and hemicelluloses (holocellulose) are generally referred to as polysaccharides. Waxes, tannins and phenols belong to extractives [4].

Natural vegetable fibres such as hemp, jute, sisal, bamboo, coir, kenaf and others have potential to be used as organic reinforcement and/or filler material in composites. Composites based on natural and fast renewable resources, especially cellulosic materials, are increasing in importance due to their numerous advantageous properties for application in sustainable building constructions [3]. Composite materials based on natural cellulosic fibres with inorganic binder represent a group of lightweight materials providing a healthy living in buildings [5].

Growing interest in using hemp hurds as waste material from bast hemp fibres production into lightweight composites is recorded in the recent years. Interesting properties such as thermal, mechanical, acoustic and antiseptic including low density, biodegradability, low costs and ecological suitability of this plant raw material predetermine its use in a function of organic filler into composite [6].

The technical hemp (Cannabis Sativa L.) is the source of two types of fibres; bast fibres and woody fibres (hurds). The properties of hemp fibres depend on their chemical composition. The bast fibres contain larger amounts of cellulose compared to the hemp hurds. On the contrary, contents of hemicelluloses and lignin as amorphous substances are higher in hurds [7].

Cellulose in hemp hurds is identified as the main structural component of the fibre, which is present mainly in the crystalline phase. Hemicelluloses and lignin present mostly in the amorphous phase, which plays an important role in controlling fibre properties. One of the key problems of successful application of plant fibres is their heterogeneity and hydrophility resulting in high moisture sorption sensitivity of biomaterial. Hydroxyl groups in the structure of cellulose, hemicelluloses and lignin are responsible for the hydrophilicity of the plant material [8]. To decrease hydrophilicity and modify cellulosic composition of hemp fibres, chemical and/or physical [9-10] treatment of the natural material surface are applied.

In this paper, the results concerning Fourier transforms infrared spectroscopy (FTIR) study of hemp hurds after physical, chemical and physico-chemical treatment in comparison to the reference sample are given.

2. Materials
In the experiments, the technical hemp hurds coming from the Dutch company Hempflax was used as organic filler into biocomposites. The used material was polydispersive with wide particle length distribution (8-0.063 mm) and its density was 117.5 kg.m$^{-3}$. These hemp hurds contain more hurds material than bast fibres. The content of polysaccharide component (holocellulose) is 77.3 %. The amounts of cellulose and hemicelluloses like holocellulose components are 42.6 and 34.7 %, respectively. Other components present in hemp are lignin (23.7%), compounds soluble in toluene and
ethanol (2.8 %) and ash (1.8 %). The structure of hemp hurd slices was examined by optical microscopy (NIKON SMZ 1500, Japan). The photomicrograph (figure 1) of hemp hurds shows compact and unfibrilled fibre structure. The presence of dirt and waxes on the material surface is observed.

For surface treatment process of hemp hurds, deionized water and sodium hydroxide (Chemapol, Slovakia, p. a.) solution were used as ultrasonic cleaning medium.

3. Methods
Prior to treatment and in order to ensure constant humidity content, fibres were dried at 80°C for 24 h in the drying oven.

3.1. Fibre surface treatment
Most of modification processes of dried hemp hurds were realized by ultrasonic treatment process for 1h. To compare the impact of physical treatment by ultrasound, the same experiments were carried out under static conditions without ultrasonic action. Deionized water, 0.1 M and 0.2 M NaOH solution, was used as a cleaning medium in the experiments. In all cases of surface treatment, the ratio s:l was 1:10. An ultrasonic bath TESON 10 (Tesla, Slovakia, 220 V, 50 Hz, 650W of power output) was used for ultrasonic cleaning process of hemp hurds. All hemp hurds samples were dried at 80°C after their treatment.

3.2. Fourier transform infrared spectroscopy
Fourier transform infrared spectroscopy (FTIR) measurements were carried out on Bruker Alpha Platinum spectrometer with Attenuated Total Reflectance (ATR) technique (BRUKER OPTICS, Germany). Total 24 scans were performed on each sample in the range of 400-4000 cm⁻¹. FTIR spectroscopy is capable of detecting structural changes in biomaterial. It provides information about the presence or absence of specific functional groups or formation of new functional groups and can give an even deeper insight into the fibre structure. FTIR allows identification of the main components of cellulose.

4. Results and discussion
FTIR spectroscopy provides information about the structure of the main components in hemp hurds. The FTIR spectra for chemically treated hemp hurds samples compared to the reference sample are shown in figure 2. As it can be seen, significant infrared spectral differences are observed in case of
hemp hurd surface modification with 0.2 M solution of NaOH. Therefore, this sample was selected for
the further FTIR spectra comparison. In figure 3, the spectra of the physical, chemical and physico-
chemically treated hemp hurds are compared with the original sample.

Figure 2. FTIR spectra of hemp hurds: reference (A); chemically modified with 0.1 M NaOH solution
(B); 0.2 M NaOH solution (C).

Figure 3. FTIR spectra of hemp hurds: reference (1); ultrasonic modified with deionized water (2);
chemically modified with 0.2 M NaOH solution (3); ultrasonic modified with 0.2 M NaOH solution (4).

Main infrared spectral differences are observed in figures 2 and 3, which allow identifying the
structural changes in lignocellulosic material after chemical, physical and physico-chemical treatment.
The changes in FTIR spectra due to all treatments of hemp hurds are shown in two regions between 3600 – 2800 cm\(^{-1}\) and 1800 to 900 cm\(^{-1}\). Peak positions corresponding to vibrations of function groups present in the studied hemp material are consistent with the literature data published for vegetable fibres [11]. The range of wave number of 3570-2900 cm\(^{-1}\) is characteristic for stretching vibration of O-H and C-H bonds in polysaccharides. Based on [12], a broad band in the spectra range of 3490 - 3170 cm\(^{-1}\) represents the complex vibrations of hydroxyl stretching of inter- and intra-molecular hydrogen bonds. For the hemp hurds sample treated in NaOH solution, the peak intensity located near 3300 cm\(^{-1}\) is less sharp (figure 2). Its intensity decreases in the case of 0.2M NaOH treatment of hemp hurds due to mercerization. The peak characteristic for waxes and oils present at 2851 cm\(^{-1}\) is present in all samples but after physico-chemical treatment is obviously less marked.

Many absorption bands corresponding to vibration of various functional groups present in hemp components are observed in the region of 1800 to 900 cm\(^{-1}\). This range was employed to characterize the structure of hemicelluloses, lignin, but mainly of cellulose. Only the most visible differences in the spectra of the treated samples compared to the reference hemp hurds are presented and discussed. One of such differences is the modification of the absorption bands in the range of 1700-1750 cm\(^{-1}\). Two signals are attributed to the stretching vibration of an unconjugated functional group of C=O or COOH, where peak 1733 cm\(^{-1}\) corresponds to hemicelluloses and 1742 cm\(^{-1}\) – to pectins and waxes [13]. These peaks have partially disappeared after treatment with NaOH in accordance with [14]. Indeed, NaOH treatment is known to remove hemicelluloses [15]. The peak at 1030 cm\(^{-1}\) belongs to C-C, C-OH, C-H ring and side group vibrations in hemicelluloses and pectin.

According to [16], lignins in hemp have most powerful absorption bands at the frequency range 1605 –1639 cm\(^{-1}\) (in our spectra 1594 – 1635 cm\(^{-1}\)). Based on the observation of the sharp peaks located at 1594 cm\(^{-1}\) and 1507 cm\(^{-1}\) (C-C stretching from aromatic ring) in FTIR spectra, ultrasonic treatment and also NaOH treatment led to partial removal of lignin. According to literature data [15], lignin cannot be totally removed by the alkaline process. As it is evident from figure 3, the peaks typical for lignin were clearly observed at 1319 cm\(^{-1}\) in all samples.

Typical bands assigned to cellulose were observed at 896 cm\(^{-1}\) and in the region of 1630 –1160 cm\(^{-1}\). The absorption band at 896 cm\(^{-1}\) is assigned as C-O-C stretching vibration of glycosidic bonds in polysaccharides. The absorption bands assigned to cellulose at 1424 and 1373 cm\(^{-1}\) come from -CH\(_2\)- and CH\(_2\) bending vibrations. The peaks at 1337 and 896 cm\(^{-1}\) represent O-H bending vibrations in cellulose. The band about 1320 cm\(^{-1}\) corresponds to -CH\(_2\)- wagging vibration, which distinguished between amorphous and crystallized cellulose [17].

5. Conclusion

The present paper is devoted to FTIR investigation of hemp hurds changes caused by chemical or physical treatment and by combination of these treatments. As it has been shown, the non-cellulosic components such as hemicelluloses, lignin and waxes after all treatment processes of hemp hurds were partially removed in dependence on the treatment procedure and operating conditions. The best result of degradation of these non-cellulosic materials was reached by physico-chemical treatment (ultrasonic alkaline treatment in 0.2 M NaOH solution).

Whereas this physico-chemical treatment is in the initial stage of research, it is necessary to carry out additional analysis (changes in chemical composition, thermal analysis, X-ray diffraction measurement) and also to study the impact of these hemp hurd treatments on the properties of biocomposites prepared with organic filler and inorganic matrix.
6. References

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