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Characterization of Cellulosic Fibers by FTIR Spectroscopy for Their Further Implementation to Building Materials

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Abstract

Nowadays, the material recycling is a growing trend in development of building materials and therefore using of secondary raw materials for production new building materials is in accordance with sustainable development in civil engineering. Therefore, it is increasingly becoming crucial to accelerate the transition from application of non-renewable sources of raw materials to renewable raw materials. One fast renewable resource is natural plant fibers. The use of the cellulosic fibers as environmentally friendly material in building products contributes to the environmental protection and saves non-renewable resources of raw materials. Wood fibers and recycled cellulose fibers of waste paper appear as suited reinforcing elements for cement-based materials. In this paper, there is used application of Fourier transform infrared spectroscopy (FTIR) on cellulose fibers coming from different sources. FTIR spectra of cellulose fiber samples are investigated and compared with reference sample of cellulose.

Keywords

Renewable Raw Materials, Cellulose Fibers, Infrared Spectroscopy

1. Introduction

The last few decades have revealed the growing interest of industry and scientists in the research and development of composite materials based on organic materials originating from renewable sources. Lignocellulosic biomass has become a promising alternative source of raw materials for industrial applications because the main component—cellulose in most plants is inexhaustible [1]. Cellulose as one of the most important polysaccharides in the plant cell wall is widely used in

the paper industry [2]. A large amount of cellulosic waste is generated yearly by the agro-industries [3].

Increasing importance of cellulosic materials utilization is due to their numerous advantageous properties for application in sustainable building constructions. Therefore, it is increasingly becoming crucial to accelerate the shift from classical to environmentally friendly materials, and so to contribute to the transition to equitable, sustainable, post fossil-carbon societies [4]. In this context, there are efforts centered upon bio-based economy based on sustainable production and consumption of renewable biological resources, as well as their conversion into bio-based products and energies. It is the possible way of achievement of sustainable development in the construction industry to shift from the limited and finite material resources to easily renewable raw material resources. The utilization of biomass in industry as a major strategic approach of 21st century is mainly focused on the development bio-based building materials. Eco-builders are interested in the utilization of natural biomass resources and recycled waste related materials/products contributing to regulation of the indoor moisture content and to greater levels of indoor air quality [5].

Ligno/cellulosic fibers obtained from biomass are attractive for their application into because of their positive environmental impact [2]. But cellulosic fibers obtained from wood are also a unique material reinforcing the cement composites. They are non-hazardous, renewable and readily available at relatively low cost compared to other commercially available fibers [6]. Due to the increasing scarcity of wood resources, the research is mainly concentrated on the utilization of cellulosic fibers obtained from waste paper as a possible and valuable resource of fibers for preparation sustainable building materials. From this point of view, recycled cellulosic fibers offer the economic advantage that can also reduce the environmental impact risks of primary production of fibers. This trend of incorporation of recycled cellulosic fibers and combination of natural and/or recycled fibers into composites with inorganic matrix is at the center of attention of researchers [7] [8] [9]. Maximizing their use in building materials and improving their performance can be achieved through properties characterization of cellulosic fibers by using adequate methods in order to reveal their chemical composition and physical properties because the composites require a strong fiber with good adhesion between matrix and fiber to enhance their final properties [6].

Fourier transform infrared spectroscopy (FTIR) is one of the most commonly used methods for identification different functional groups constituting a compound. FTIR is a rapid and non-destructive technique for the qualitative and quantitative determination of biomass components in the mid-IR region [10]. FTIR spectroscopy provides information about molecular fragments, the presence or absence of specific functional groups and can give an even deeper insight into the fibers structure. FTIR with ATR unit allows attenuation of the incident radiation and provides IR spectra without the water background absorbance [11].

The aim of this paper is comparative FTIR investigation of cellulosic fibers from wood pulp and recycled waste.

2. Materials and Method

2.1. Materials

Two kinds of cellulose fibers from different processing (wood processing—the sulphate bleached beech tree cellulose; GW500, W640 and G250WT) and (recycling waste paper as newspapers, magazines, and cartons; G500T, G700T and G3/00T) were provided by Greencel Ltd (Hencovce, Slovakia). Figure 1 illustrates represent samples of each kind of cellulosic fibers that are different in color (white—bleached wood pulp) and (grey—recycled fibers).

Six samples of cellulose fibers were tested. Their physical and chemical properties are shown in Table 1. Average fiber length as well as width was measured by L&W Fiber Tester (Lorentzen & Wettre, Sweden). Around 20,000 fibers were measured from each pulp in each test (the tests were performed in triplicate). Aspect ratio is characterized as ratio of average fiber length to width. Dry matter was 93% in all samples except G250WT sample. pH value of samples ranges from 6 to 7.5.

The first set of samples featured with high content of holocellulose and low lignin and ash content compared to recycled fibers. Chemical analysis of components of cellulosic fibers is described in our previous paper [12]. As comparative material for FTIR study was used synthetic microcrystalline cellulose.

2.2. Method

Infrared spectroscopy combined with the ATR technique (Attenuated Total Reflectance) is ideal for the investigation of the IR of solids without any sample preparation. ATR spectroscopy, also known as internal reflection spectroscopy, is a versatile and non-destructive technique that can be used to measure the IR-spectrum. To perform the analysis, the sample is placed in contact with the

Figure 1. Greencel cellulosic fibers: white wood pulp and grey recycled fibers.

Table 1. Physical and chemical properties of cellulose fibres.

Cellulose Samples	Properties of Cellulose Fibers								
	Bulk density [kg/m^3]	Max. length [μm]	Average fiber length [μm]	Average fiber width [μm]	Aspect ratio	Holocellulose [%]	Cellulose [%]	Lignin [%]	Ash [%]
GW500	60 - 80	500	504	21.7	23.2	99.11	81.99	0.42	0.08
W640	35 - 45	1000	640	21.3	30.0	99.67	80.49	0.05	0.21
G250WT	80 - 100	500	514	21.8	23.6	99.09	62.13	0.12	12.11
G500T	50 - 100	400	556	29.5	18.8	71.03	47.40	17.05	19.91
G700T	40 - 70	600	701	30.9	22.7	71.98	46.95	20.05	22.80
G3/00T	30 - 50	1200	796	29.0	27.5	81.30	56.97	20.11	16.54

surface of an IR transmitting crystal. The IR light is reflected from the inside surface of the crystal, but it penetrates a small distance into the sample and is therefore partially absorbed.

No sample preparation is needed and the only requirement being that the sample is in intimate contact with the crystal surface.

FTIR spectra of cellulose fibres from wood pulp and recycled fibres were obtained on an Alpha Bruker Platinum—ATR spectrometer in the range from 4000 cm^{-1} to 400 cm^{-1} at a resolution of 4 cm^{-1}. A total of 24 scans were taken for each sample. The spectra of samples were compared with microcrystalline cellulose (MC).

3. Results and Discussion

FTIR spectra of cellulose fibers from wood pulp and recycled waste paper are compared with reference sample in **Figure 2** and **Figure 3**. The absorption bands are observed in two wave number regions of 3660 - 2800 cm^{-1} and 1650 - 400 cm^{-1}. The presence of peaks on the spectra of cellulose samples coming from wood pulp corresponds to bands of microcrystalline cellulose (**Figure 2**), while differences in absorption bands intensities and appearance of new peaks in spectra of recycled cellulosic fibers are observed.

Identification of the absorption bands is following. The observed peaks in the wave number range of 3660 - 2900 cm^{-1} is characteristic for stretching vibration of O-H and C-H bonds in polysaccharides. The broad peak at 3331 cm^{-1} is characteristic for stretching vibration of the hydroxyl group in polysaccharides [3] [13]. This peak includes also inter- and intra-molecular hydrogen bond vibrations in cellulose [14]. The band at 2894 cm^{-1} is attributed to CH stretching vibration of all hydrocarbon constituent in polysaccharides [3] [13]. Typical bands assigned to cellulose were observed in the region of 1630 - 900 cm^{-1}. The peaks located at 1633 cm^{-1} correspond to vibration of water molecules absorbed in cellulose [3] [13]. The absorption bands at 1428, 1367, 1334, 1027 cm^{-1} and 896 cm^{-1} belong to stretching and bending vibrations of -CH_2 and -CH, -OH and C-O bonds in cellulose [10] [15]. The band at around 1420 - 1430 cm^{-1} is

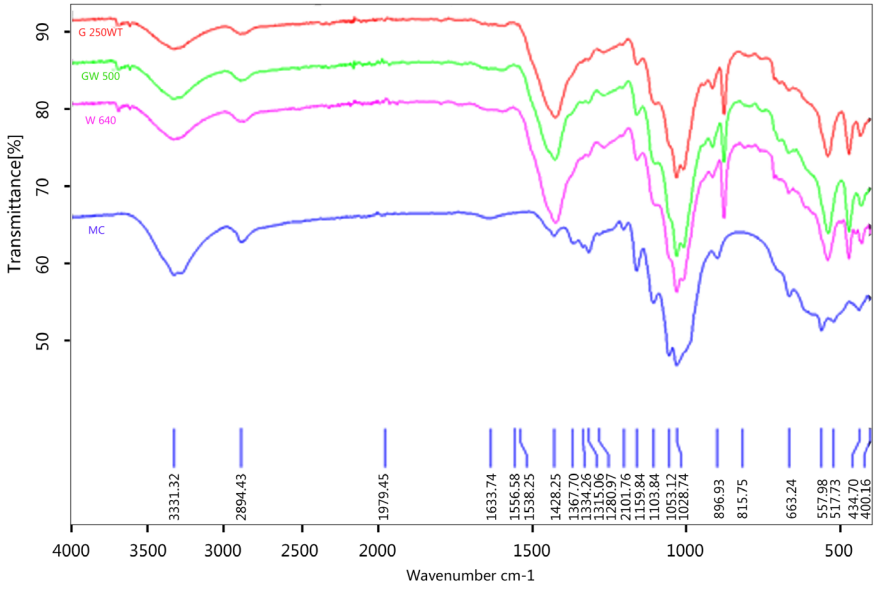

Figure 2. FTIR spectra of wood pulp cellulose fibers compared to microcrystalline cellulose (MC).

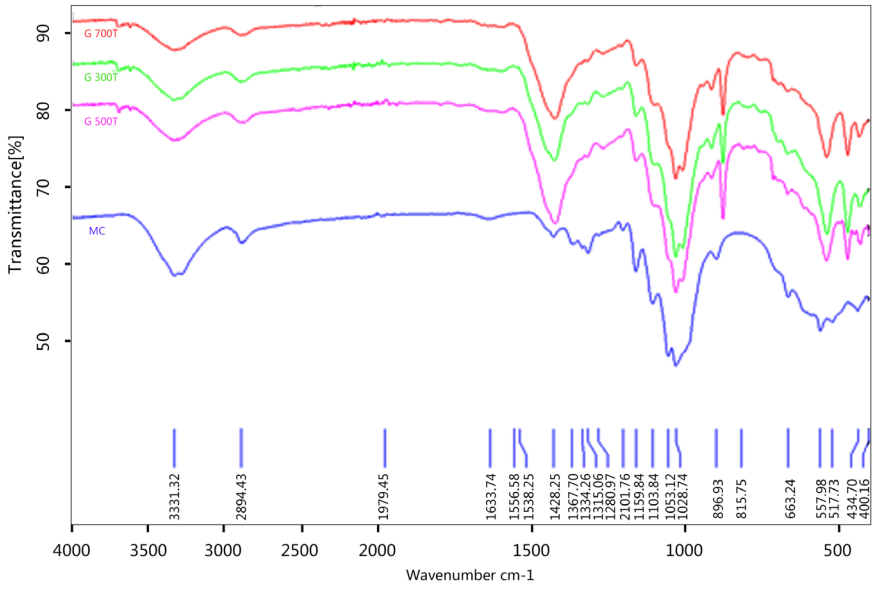

Figure 3. FTIR spectra of recycled cellulose fibers compared to microcrystalline cellulose (MC).

associated with the amount of the crystalline structure of the cellulose, while the band at 897 cm^{-1} is assigned to the amorphous region in cellulose [1].

In Figure 2, visible differences were noted in the spectrum of G250WT sample. There are changes in intensities of the signals at 1428 cm^{-1}, 896, 875 cm^{-1} and 712 cm^{-1}. A broad peak at 1428 cm^{-1} includes -CH_2 and CH bonds vibrations coming from cellulose as well as the vibration of C = O bonds in the carbonate ion (CO_3^{2-}). The CO bond vibrations in pure $CaCO_3$ are visible at 1475 cm^{-1}. The weak intensity peaks at 875 and 712 cm^{-1} also belong to C=O bonds in

carbonate anion. The FTIR spectra of the cellulosic fiber samples from waste paper in **Figure 3** are very similar to spectrum of G250WT sample (**Figure 2**). This fact implies the presence of calcium carbonate [11] in cellulose samples as impurity deriving from the used filler in paper making what corresponds to cellulose purity (**Table 1**). However, further new peaks attributed to kaolinite in the spectra of recycled fibers were observed. The structure of this aluminosilicate mineral is two-layered, one silicon-oxygen tetrahedral layer (SiO_4) joined to $Al(O,OH)_6$ octahedral layer or expressed in other way, $[Si_2O_5]_2$-layer and $[Al_2(OH)_4]_2$-layer with pseudo-hexagonal symmetry [16]. The four absorptions at 3697, 3669, 3645 and 3620 cm^{-1} are typical for kaolinite spectrum (amount aluminum in octahedral). The band at around 3620 cm^{-1} has been ascribed to the inner hydroxyls, and the peaks at around the other three characteristic wave numbers are generally attributed to vibrations of the external hydroxyls. The absorption bands observed at 3420 - 3445 cm^{-1} and at 2894 and 1633 cm^{-1} could be assigned to the OH vibration mode, which are observed in almost all the natural hydrous silicates. However, the H-O-H bending of water is observed at 1620 - 1642 cm^{-1} [17]. In the region of 1000-500 cm^{-1}, vibration of the main functional groups of Si-O and Al-OH were observed. The band at around 1100 - 1010 cm^{-1} is assigned to Si-O stretching vibrations and the absorption bands at 914, 540 and 470 cm^{-1} are attributed to Si-O-Si bending vibration.

The doublet at 780 - 798 cm^{-1} is due to Si-O-Si inter tetrahedral bridging bonds in SiO_2. The peaks identified at 936-914 cm^{-1} correspond to Al-OH bending vibration in kaolinite [17] [18] [19]. The above-mentioned facts about the presence of calcium carbonate and kaolinite as impurities in cellulose samples confirm their origin from the used filler in paper making what corresponds to cellulose purity (**Table 1**).

4. Conclusion

This work presents the results of FTIR spectroscopic comparative study of two kinds of cellulosic fibers with reference sample of microcrystalline cellulose. Studying the chemical composition and FTIR spectra of six samples of cellulosic fibers from wood pulp and waste paper showed differences in organic components contents such as cellulose, hemicelluloses and lignin as well as in the presence of inorganic impurities (calcite and kaolinite) originating from filler in paper making. More detail characterizations of cellulose samples by using XRD, TG/DSC and SEM will be a subject of further research work.

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