Changes in thermal stability of lignocelluloses waste aggregates long-term incorporated in composite

N Stevulova¹ and A Estokova¹

¹Institute of Environmental Engineering, Faculty of Civil Engineering, Technical university of Kosice, Vysokoskolska 4, 042 00 Kosice, Slovakia

Abstract. This paper is addressed to comparative study of changes in thermal stability of surface-modified hemp-hurds aggregates long-term incorporated in bio-aggregate-based composites with the original ones before their integration into alternative binder matrix. In this study, the effectiveness of alkaline treatment of hemp hurds compared to the raw bio-aggregates as well as in relation to their behaviour when they are long-term incorporated in the MgO-cement environment is investigated. The differences in the thermal behaviour of the samples are explained by the changed structure of hemp hurds constituents due to the pre-treatment and long-term action of the alternative binder components on the bio-aggregates. Alkaline treatment increases thermal stability of hemp hurds compared to raw sample. Also long-term incorporation of hemp hurds in MgO-cement matrix had a similar effect in case of alkaline modified bio-aggregates. The more alkali ions present in the structure of hemp hurds samples, the more ash is formed during their thermal decomposition studied by thermal gravimetry (TG) and differential scanning calorimetry (DSC).

1. Introduction
Biomass as a fast renewable organic material derived from plants and produced by the agricultural sector serves mainly as energy source [1]. However, agricultural residues produced in large amounts from the crops and forest wastes are alternative raw material source in many sectors [2]. More recent strategies have been developed to achieve the sustainability in construction industry in changing climate conditions and to utilize bio-resources in building materials production. The use of waste bio-aggregates into environmental friendly bio-based composites has drawn an increasing interest due to environmental benefit, and performing waste management. Attractive structure of waste bio-aggregates, their good mechanical properties, biodegradability, non-toxicity, and low carbon footprint has become a challenge and motivation for many researchers [3-7]. These specific properties make lignocellulosic material an attractive alternative lightweight filler component in bio-aggregate-based composites with inorganic matrix [8].

One of the most studied waste bio-aggregates are hemp hurds coming from industrial hemp (Cannabis Sativa L.) cultivated mainly for its valuable bast fiber and seeds. Hemp fiber processing leads to great amounts of waste hemp hurds originating from a large proportion of the stalk and stem of this plant [9]. Hemphurds (HH) is the inner woody core of the stem opposite its outer part which is formed by bast fibres. From a chemical point of view, HH is lignocellulosic material. Cellulose and hemicellulose have the largest proportion of about 70% in bio-aggregates. Cellulose as the main constituent of HH is encapsulated by the lignin-hemicellulose matrix [10].

As known, the structural complexity, heterogeneity of HH, surface impurities, large amount of hydroxyl groups in the structure, and their high moisture sorption sensitivity cause the chemical degradation of the bio-aggregate structure when incorporated in cementitious binder-bonded
HH embedding in an alkaline environment of binder leads to dissolution of amorphous components of lignocellulosic materials (lignin and hemicellulose), and hydrolysis of cellulose molecules during the setting and hardening processes ongoing at aggregate-binder interfacial zone in bio-based composite. The mechanisms affect the kinetics of binder hydration [11], it results in a weaker adhesion bio-aggregates to binder particles at their interface in the hardened composite. To eliminate the disadvantages of lignocellulosic bio-aggregates and to improve their adhesive performance with the matrix particles in composite and thermal stability, pre-treatment methods are used. In our works, the great attention has been devoted to the comparative study of properties of chemically and physico-chemically modified HH [12,13] and final technically important parameters of hardened bio-based composites with MgO-cement [14-16]. Knowledge of physical and mechanical properties of composites is relatively extensively described, but there is not paid a sufficient attention to the stability study of organic material incorporated in the matrix for a long time. Therefore, this paper provides comparing the thermal behavior of the raw and surface-modified hemp aggregates before and after their long-term incorporation in MgO-cement matrix. The aim is to determine the effect of qualitative changes in hemp hurdsbio-aggregates on their thermal stability.

2. Materials and Methods

2.1. Bio-aggregates

Four hemp hurds samples were used in this study. The raw bio-aggregate sample (RHH-reference sample) consisted of a large majority of hemp hurds over hemp bast fibers. The Netherlands Company HempFlax (Oude, Pekela) supplied this lightweight waste material (density of 117.5 kg.m$^{-3}$). It is characterized by a wide particle size distribution of particles (8–0.063 mm). Chemically treated hemp hurds(AHH) in 5M NaOH solution was used [12]. Contents of cellulosic and non-cellulosic components in an oven-dried raw and alkaline treated HH in 5M NaOH solution are given in Table 1. The reference and alkaline treated HH excluded from the composite samples (RHH_AB and AHH_AB) after their long-term incorporation (6 years) under laboratory conditions (temperature 23±2 °C; relative humidity 65±5 %) were investigated. Bio-based composites were prepared from 40 vol. % of bio-aggregates, 29 vol. % of MgO-cement (consisting of the same portion of MgO, SiO$_2$ and NaHCO$_3$ components) and 31 vol. % of water.

Table 1. Chemical composition of raw and alkaline treated HH samples.

| Hemphurds sample Designation | Cellulose (%) | Hemicellulose (%) | Lignin (%) |
|-----------------------------|---------------|-------------------|------------|
| Raw (reference) RHH         | 44.5          | 32.8              | 22.0       |
| NaOH treated AHH            | 53.9          | 12.1              | 27.4       |

2.2. Thermal analysis

The thermal decomposition of HH constituents in the samples was investigated by a TG/DSC system using a model STA 449F3 (Netzsch, Germany). Sample amount of 10 ± 2 mg was loaded in alumina cup to DSC/TG holder and heated at a heating rate of 10 K/min from 25 to 900 °C under air flow of 60 mL.min$^{-1}$. The maximum thermal degradation temperature was obtained from the derivative thermogravimetric (DTG) data.

3. Results and Discussion

The thermal behaviour and stability of the original raw (RHH) and alkaline treated sample (AHH), and hemp hurds samples excluded from long-term hardened composites (RHH_AB; AHH_AB) were determined by TG, DTG and DSC curves (Figures 1-3). The maximum temperature, temperature ranges, and the mass loss as a function of increasing temperature of studied samples during the hemp hurds components decomposition are given in Tables 2 and 3. The measured temperatures of decomposition in this study correspond with the known decomposition temperatures of
hempfibres/aggregates. DTG curves for all HH samples display two main mass losses related to cellulose and non-cellulosic substances except for small mass losses connected with water release. The DSC curves of HH samples indicate three thermal effects. An initial mass loss during endothermic process of the gradual evaporation of moisture is observed at low temperature (below 100 °C) on DSC curves of RHH and AHH (Figure 2b and 3b). The higher maximum temperature of this peak for alkaline treated sample AHH (74 °C) compared to RHH (63 °C) is found in accordance with published works [13, 17] and it corresponds to the water release. On the other hand, a relatively wide endothermic peak with presence of a narrow band was appeared at temperature below 130 °C on DSC curves of HH samples excluded from composites (RHH_AB and AHH_AB). The first peak is observed at lower temperatures, similar to the bio-aggregate itself, while the second band at temperatures 93.8 °C and 133.7 °C is probably related to the release of crystalline water from structure of HH sample of long-term incorporated in composite. The peak intensity significantly higher for the AHH_AB sample corresponds to the heat of 54.5 J/g compared to RHH_AB sample (39.9 J/g). The higher mass loss at lower temperature was found in AHH and AHH_AB samples indicating the evaporation of greater amount of moisture in treated and long-term incorporated bio-aggregates in composite due to presence water molecules in pores of hemp hurds.

Figure 1. DTG curve of raw (RHH) and alkaline treated hemp hurds (AHH).

Table 2. Maximum temperature $T_{\text{max}}$ of endothermic process of HH degradation and corresponding mass losses.

| Sample   | $T_{1\text{max}}$ (°C) | $T_{2\text{max}}$ (°C) | Mass loss (%) |
|----------|------------------------|------------------------|---------------|
| RHH      | 63                     | -                      | 4.99          |
| RHH_AB   | 59.4                   | 93.8                   | 7.35          |
| AHH      | 74                     | -                      | 5.21          |
| AHH_AB   | 74                     | 133.7                  | 8.97          |
Figure 2. DTG curve (a) and DSC detail (b) of raw hemp hurds (RHH) and bio-aggregate sample excluded from long-term hardened composites (RHH_AB).

Figure 3. DTG curve (a) and DSC detail of alkaline treated hemp hurds (AHH) and bio-aggregate sample excluded from long-term hardened composites (AHH_AB).

Table 3. Maximum temperature $T_{\text{max}}$ of exothermic process of HH degradation and corresponding mass losses.

| Sample  | 1st peak ($^\circ$C) | 2nd peak ($^\circ$C) | Mass loss (%) | Residuum (%) |
|---------|---------------------|---------------------|---------------|--------------|
| RHH     | 284                 | 332                 | 61.83         | 7.67         |
| RHH_AB  | 242                 | 284                 | 40.10         | 19.65        |
| AHH     | 292                 | 354                 | 63.92         | 10.74        |
| AHH_AB  | 258                 | 360                 | 45.01         | 23.99        |

A second significant mass loss occurring in two exothermic processes from approximately 150 to 600$^\circ$C with peak around 332 $^\circ$C and 354 $^\circ$C (RHH and AHH) and 284 $^\circ$C and 360 $^\circ$C (RHH_AB and AHH_AB) is due to the decomposition of the three major constituents of the lignocellulosic aggregates, namely cellulose, hemicelluloses and lignin [18]. Also pectin as minor constituent of HH is released in this temperature range. As known [13], thermal degradation of HH constituents in air atmosphere takes place simultaneously due to the complexity of hemp hurds microstructure. Therefore, distinguishing the decomposition temperature of the individual HH components is difficult. The shoulder visible on the DTG curves of hemp hurds samples (Table 2) is attributed to the
hemicellulose and lignin decomposition and the second peak at higher temperatures corresponds to cellulose decomposition and lignin. The onset of decomposition of hemp hurds occurs at 150°C in accordance with [19]. It is associated with the simultaneous depolymerization of majority of hemicelluloses and pectin up to 350 °C. Pectin is degraded about 280 °C. However, cellulose decomposition occurs with rapid mass loss in temperature range 300-360 °C. This process is characterized by ongoing three primary reactions: thermo-oxidation, dehydration and depolymerisation in the temperature range of 120-350 °C [20]. Thermo-oxidation and dehydration are driven by diffusion processes and run mainly in amorphous phases of polysaccharides. The oxidation of hydroxyl groups in cellulose molecules running during heating in air atmosphere results in the increasing number of carbonyl groups. Cellulose depolymerisation occurs primarily through random cleavage of the glycosidic bonds. Lignin degradation proceeds slower and gradually over a broad temperature range than two components of holocellulose. As shown in [21], a partial decomposition of lignin occurs in temperature range of 250–500 °C. As shown in Table 3, the thermal stability of AHH sample increased due to alkaline treatment. The partial removal of hemicellulose and lignin covering cellulose fibres exposes more cellulose hydroxyl groups to alkali ions. The alkali sensitive OH groups present in the hemp hurds constituents molecules are broken down and replaced with less hydrophilic O–Na+ groups between the cellulose molecular chains[22]. As shown in [12,13], FTIR results confirmed a reduction OH bonds and non-cellulosic materials as well as increase in crystallinity of cellulose contributing to an enhancement of the thermal stability after alkali treatment of hemp hurds. Degree of cellulose polymerization (DP) as a key factor determining the number units in the chain, affecting thermal stability of cellulose [23] and the accessibility of hydroxyl groups for their participation in the reaction with Na+ ions. Decrease in DP value was recorded for AHH sample (585) in comparison to RHH (1,302) [13]. Also long-term incorporation of hemp hurds in MgO-cement matrix showed a similar effect in case of alkaline modified bio-aggregates. Cellulose degradation peak in sample AHH_AB is moved to slightly higher temperature (360 °C) compared to AHH sample (354 °C). The sum of the mass losses achieved after hemp hurds constituents decomposition in RHH and AHH samples at the temperature of 398°C in air corresponds to values of 62-64%. When compared to the holocellulose content in these samples (77.3 and 66 %), cellulose has not yet completely degraded and its decomposition continues. The more alkali ions present in the structure of hemp hurds samples, the more ash is formed during their thermal decomposition. As expected, lower mass losses (40.1 and 45.01%) at this degradation process were found for HH samples long-term incorporated in composites due to inorganic substances present on the surface and in the pore volume of the bio-aggregates. Also values of residuum found at 898 °C correspond to the above mentioned fact. The ash content of AHH is higher (10.64%) than that of RHH (7.67 %). Also the same trend is observed for samples long-term incorporated HH samples (19.64 and 23.99%).

4. Conclusion
In this study, TG and DSC analyses have been carried out for the thermal stability finding of raw and alkaline treated hemp hurds before and after their long-term incorporation in composite based on alternative binder matrix of MgO-cement. To this purpose, 6 years’ composites with embedded raw plant waste bio-aggregate and product surface modified with NaOH have been used. Changes in thermal behavior of hemp hurds samples excluded from MgO-cement matrix were compared. The conclusions can be drawn as follows:

- The results obtained from detailed analysis of TG, DTG and DSC curves of raw and alkaline treated hemp hurds confirmed a partial degradation of hemp hurds constituents (hemicellulose and lignin) induced by surface modification by using NaOH treatment. The shift to higher decomposition temperature of cellulosic components demonstrates the better thermal stability of AHH sample.
- The evaluation of the long-term incorporated NaOH treated hemp hurds excluded from composite confirmed also its better thermal stability compared to raw HH due to the formation
of less hydrophilic O-Na\(^+\) groups between the cellulose molecular chains related to alkali surface modification of bio-aggregates and effect of the alkaline component of MgO-cement.

- These results underline the need to further investigate specific treatments of hemp hurds in response to their behavior exhibited by binder matrix.

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