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Changes in the Properties of Composites Caused by Chemical Treatment of Hemp Hurds

N. Stevulova, I. Schwarzova

***Abstract*—**The possibility of using industrial hemp as a source of natural fibers for purpose of construction, mainly for the preparation of lightweight composites based on hemp hurds is described. In this article, an overview of measurement results of important technical parameters (compressive strength, density, thermal conductivity) of composites based on organic filler - chemically modified hemp hurds in three solutions (EDTA, NaOH and $Ca(OH)_2$) and inorganic binder MgO-cement after 7, 28, 60, 90 and 180 days of hardening is given. The results of long-term water storage of 28 days hardened composites at room temperature were investigated. Changes in the properties of composites caused by chemical treatment of hemp material are discussed.

***Keywords*—**Hemp hurds, chemical modification, lightweight composites, testing material properties.

I. Introduction

INORGANIC bonded hemp hurds composites are perspective, environmentally friendly materials based on natural and fast renewable raw material from agriculture. In recent years, considerable efforts have been made to develop natural fiber-reinforced composites for sustainable and available structures. However, the long-term durability of natural fiber-reinforced composites may be limited due to their high permeability and lack of resistance to grow of crack, particularly fibers obtained from agricultural by-products [1], [2].

In recent years, when industrial hemp cultivation was legalized in European countries, many research projects have been oriented to the using hemp as a good reinforcement component with high tensile strength in building materials with emphasis to identify possible applications for hemp composites. The effect of using different binding agents in combination with hemp fibers in composites was examined in many research works [3], [4].

The technical hemp (*Cannabis sativa* L.) is the source of two types of fibers; bast fibers (about 35%) and woody fibers, called shives or hurds (about 65%). Structure of hemp stem is very complicated. Bast fibers are situated under epidermis covering the hemp stem and hurds are inside the hemp stem. The fiber content is given in relation to the weight of whole stem [5]. The properties of hemp fibers depend on the fiber chemical composition. The bast fibers contain more amounts of cellulose compared to the hemp hurds. Contrary, contents of hemicellulose and lignin as amorphous substances are higher in hurds [6]. The lightweight composites were developed by using only hemp fibers. The most of the researches are currently focused to the use of the woody core part of the hemp (hurds) as waste material from hemp fiber separation process. Only 5% of hemp hurds is used in preparation of building materials [7], mainly in the production of thermal insulation composites due to their porous structure. The properties of biocomposites depend on chemical composition and structure of hemp material, matrix properties as well as good adhesion in the hemp fibers (hurds) – matrix interface. Therefore, the surface treatment procedure of the hemp fibers/hurds is used for the improvement of the adhesion in the fibers – matrix interface [8].

In the experimental study [9], the parameters affecting to the physical and mechanical properties of hemp composite based on conventional and alternative binders was performed. The properties of chemically treated hemp hurds were investigated in paper [10].

In this paper, an overview of the results concerning the testing of physical and mechanical properties of lightweight composites based on unmodified and chemically modified hemp hurds and nonconventional binder MgO-cement after their hardening in indoor conditions. The results of measured parameters (density, water content, compressive strength, thermal conductivity coefficient) of prepared composites are presented in dependence on a hardening time. Kinetic study of long-term water storage of 28 days hardened composites at room temperature was also performed.

II. Material and Methods

A. Material

The technical hemp hurds slices (*Cannabis sativa* L.) coming from the Netherlands company Hempflax were used in experiments.

This hemp hurds contains more hurds material than bast fibers. The used hemp material was polydispersive with a wide mean particle length distribution (8-0.063mm) and its density was 117.5 $kg \cdot m^{-3}$. The average moisture content of the hemp material determined by weighing of hemp sample before and after drying at 105ºC for 24h was found out 10.78 wt.%. A milled and oven-dried sample was used for the determination of chemical composition of hemp hurds.

The chemical composition of used hemp hurds is shown in Table I.

The content of holocellulose was determined by using the modified method according to Wisea. The quantitative

N. Stevulova is with Technical University of Kosice, Faculty of Civil Engineering, Institute of Environmental Engineering, Vysokoskolska 4, 042 00 Kosice, Slovak Republic (phone: 00421-55-6024126; e-mail: nadezda.stevulova@tuke.sk).

I.Schwarzova is with Technical University of Kosice, Faculty of Civil Engineering, Institute of Environmental Engineering, Vysokoskolska 4, 042 00 Kosice, Slovak Republic (e-mail: ivana.schwarzova@tuke.sk).

determination of cellulose was performed by the Kürschner-Hoffer nitration method. The content of acid-insoluble (Klason) lignin was carried out by two-step hydrolysis of polysaccharides portion in sulphuric acid. Total ash content (mineral substances) was measured by combustion of sample and subsequent annealing. Toluene-ethanol extract containing mainly extractable waxes, fats, resins as well as water extractives was obtained by extraction in a Soxhlet apparatus for 6–8h at 90°C.

MgO-cement, as a binder used in experiments, consists of caustic magnesite obtained by low temperature decomposition of natural magnesite (CCM 85, Slovakia), silica sand (Slovakia) with the dominant component of SiO2 (95-98%) and sodium hydrogen carbonate (p.a). MgO has been milled in order to reduce its particle size. Dry milling was carried out in laboratory vibratory mill VM 4 for 5min [11].

TABLE I
CHEMICAL COMPOSITION OF HEMP HURDS SLICES

Chemical composition of hemp hurds	(%)
Toluene ethanol extract	3,5
Lignin	24,4
Cellulose	44,2
Hemicellulose	30,3
Ash	1,4

B. Chemical Treatment

The chemical modification of dried hemp hurds was made by three different solutions: sodium hydroxide (NaOH) p.a. (CHEMAPOL, Czechoslovakia), calcium hydroxide ($Ca(OH)_2$) ≥96%, pulv. (ROTH, Germany), ethylenediamintetracetic acid (EDTA) p.a. (GAVAX s.r.o., Slovakia). The specifications of the chemical treatment are described in the paper [10].

C. Preparation of Composite Specimens

Experimental mixtures were prepared according to the recipe consisted of 40 vol. % of hemp hurds (unmodified as a referential material and chemically treated), 29 vol. % of MgO-cement and 31 vol. % of water. The components of mixture were homogenized in dry way and then mixed with water addition. Standard steel cube forms with dimensions 100 mm x 100mm x 100mm were used for preparation of samples. The specimens of lightweight composites were cured for 2 days in an indoor climate and then were removed from the forms. Curing was continued under laboratory conditions during 7, 28, 60, 90 and 180 days.

D. Water Absorption Tests

The dried cube specimens of composites based on original and chemically modified hemp hurds after 28 days of hardening were immersed in deionised water bath (PE closed container) at laboratory temperature (23°C) for different time durations to study their durability. After that immersion, the specimens were taken out from the water and water from all surfaces of bodies has been removed by a clean dry cloth. The specimens were reweighed after long term storage (1h – 180d). Content of absorbed water in composites after immersion time t (M_t) was calculated by the weight difference between the samples immersed in water and dry composite samples. Water absorption kinetic model published in paper [12] was used to describe the sorption curves for composites based on natural fiber (1):

$$\frac{M_t}{M_\infty} = kt^n \tag{1}$$

In (1) M_t, M_∞, are water contents at time t and at equilibrium; k and n are constants giving some information about mechanism of diffusion taking place inside composites. Both of the coefficients, n and k were calculated from experimental data using classical method of the mathematical statistics, as regression analysis, correlation analysis and testing of hypotheses.

First, the coefficient n was determined as a slope of sample regression line created by log of experimental set of data and verified by its coefficient of correlation. Using the method of testing of hypotheses was proved that this corresponding coefficient of correlation between both sets, experimental and computed data is statistically significant.

Second, the coefficient k was determined using the assumptions about the existence of a saturation point during process of absorption in time. Then this fact enables to find the asymptotic line of the corresponding process of absorption also using the method of regression analysis mentioned above.

E. Testing Methods

Density, thermal conductivity, compressive strength and water content were measured on dried and cured specimens under laboratory conditions.

The density was determined in accordance with standard STN EN 12390-7 [13].

The thermal conductivity coefficient of samples as the main parameter of heat transport was measured by the commercial device ISOMET 104 (Applied Precision Ltd., Germany). The measurement is based on the analysis of the temperature response of the analyzed material to heat flow impulses. The heat flow is induced by electrical heating using a resistor heater having direct thermal contact with the surface of the sample.

The compressive strength of all composites was determined using the instrument ADR 2000 (ELE International Ltd., England). The mean value of compressive strength of each specimen was calculated as the average of the three measured values.

The water content was determined in accordance with standard STN EN 12087/A1 [14].

III. RESULTS AND DISCUSSION

The growth of compressive strength on the time of hardening of composite samples based on unmodified and chemically modified hemp hurds is shown in Fig. 1. The values of compressive strength of composites with MgO-cement as a binding material were varied from 1.05 to 6.94

MPa when the density was ranged from 1050 to 1230 kg.m^{-3}. As Fig. 1 shows, the progression in the values of this mechanical parameter was observed in dependence on hardening time for all composites. The highest compressive strengths in each time of hardening were recorded for referential composites (based on untreated hemp hurds). Compressive strength values of composites with modified hemp hurds were in a range from 1.05 to 2.75 MPa in dependence of hardening time and density were varied from 1065 to 1230 kg.m^{-3}. Among the hardened composites based on chemically modified hemp hurds, specimens with hemp hurds treated by hydrated lime reached the highest values of compressive strength which were in the range of 1.2 to 2.75 MPa. But the measured strength values for composites with NaOH treated hemp hurds (1.07-2.3 MPa) are not significantly different from those that have been measured for composites based on the filler modified by hydrated lime. In the case of 180 days hardened composites based on NaOH treated hemp hurds, the value of compressive strength represents 83.6 % of that which was determined for composite with filler modified by hydrated lime.

These differences are probably caused by saturation of calcium ions to the surface of the hemp hurds slices [15] and creating a stronger bond between the surface of filler particles and of the matrix.

The chemical treatment of hemp hurds did not lead to improvement of mechanical properties of composites as it was expected. Cause of this phenomenon can be in a nature of used binder and surface properties of filler which led to poor interaction of binder particles and hemp hurds slices.

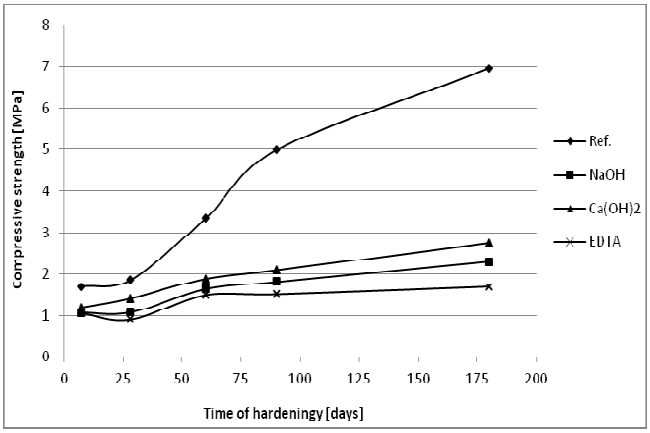

Fig. 1 Dependence of compressive strength of composites with referential and chemically modified hemp hurds on the time of hardening

The measured values of thermal conductivity coefficient of composites with unmodified and chemically modified hemp hurds (after hardening time of 28, 60 and 90 days) were varied from 0.058 to 0.11 W.m^{-1}.K^{-1} in determined interval of density values. These values were lower than values of thermal conductivity of hemp composites with lime binder [16].

The values of thermal conductivity coefficients vs. density of the studied composites are shown in Fig. 2. From the observed variance of the measured values is not possible to infer some relevant conclusions. It seems that in terms of values of thermal conductivity coefficient (0.058-0.072 W.m^{-1}.K^{-1}) in a relatively narrow range of density values (1100-1185 kg.m^{-3}) are the most favourable composites with hemp hurds treated in NaOH solution differences are probably caused by saturation of calcium ions to the surface of the hemp hurds slices [15] and creating a stronger bond between the surface of filler particles and of the matrix.

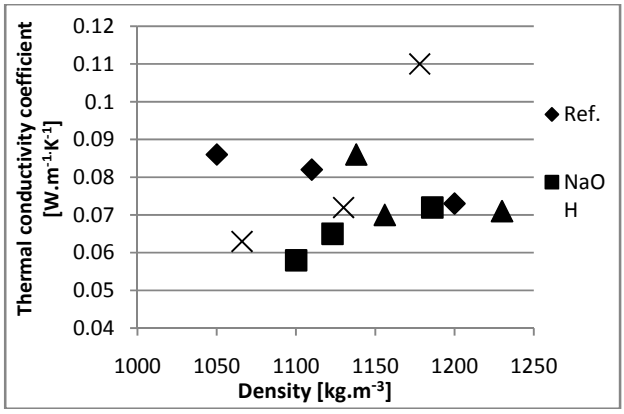

Fig. 2 Thermal conductivity coefficient vs. density of the composites with referential and chemically modified hemp hurds

Study of the influence of long water storage of 28 days hardened composites based on untreated and chemically modified hemp hurds on the mechanical properties showed decrease of the values of compressive strength [17], [18]. In the case of composites with untreated hemp hurds, the most significant decrease was observed owing to high water sorption ability of original hemp hurds in composite.

As it can be seen in Fig. 3, water content in specimens based on unmodified and modified hurds is increasing with a prolonged immersion time of composites in water. The lower saturation water content is observed for the specimens prepared with chemically modified hemp hurds slices. Surface treatment of hemp hurds slices affects the water absorption rate of composites. Kinetic of sorption and the maximum value of water absorbability (M_∞) of composites are influenced by the nature of the surface of hemp hurds. The following order of composites based on original and chemically modified hemp hurds in terms of the maximum value of M_∞ was found: Referential > $Ca(OH)_2$ > EDTA ≈ NaOH.

The calculation of the values of coefficient n according to (1) showed that coefficient n is ranged from 0.051 to 0.173 what indicates that the water absorption process takes place by the anomalous diffusion [19]. This process is characterized by the increase of a boundary between the outer parts of hemp hurds slices and the inner spaces between bundles of fibers and fibrils.

Sorption behaviour of the composites based on chemically modified hemp hurds is related to the surface treatment of organic filler which led to a change in the chemical composition of hemp hurds, especially in the degradation degree of polymerization of cellulose [20]. The most

significant changes in the contents of major components in hemp hurds (cellulose, hemicellulose and lignin) and in average degree of cellulose polymerization were recorded in the case of alkaline modification of hemp hurds by NaOH. These results are in accordance with above mentioned data of sorption behaviour of composite prepared with NaOH modified hemp hurds. As Fig. 4 shows, the maximum value of water content in composites increases with increasing average degree of cellulose polymerization.

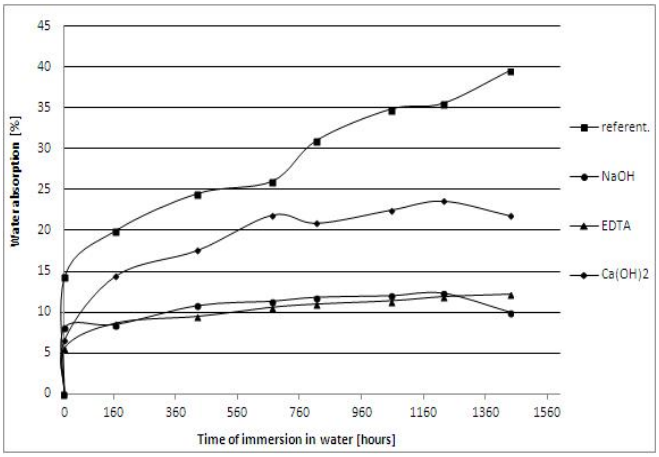

Fig. 3 Dependence of water content in composites based on chemically treated hemp hurds on the time of their immersion in water

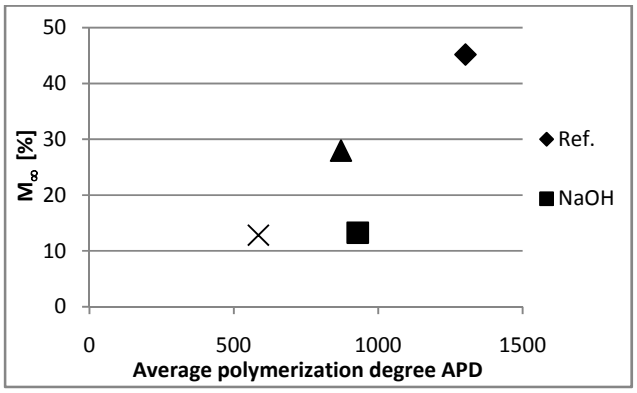

Fig. 4 Maximum value of water absorbability M_∞ of composites based on unmodified and chemically modified (in NaOH, $Ca(OH)_2$, EDTA) hemp hurds vs. average polymerization degree of cellulose

IV. Conclusion

The results show that the chemical modification of hemp hurds has an impact on some physical properties and strength parameter of hardened biocomposites prepared with MgO-cement as a binder.

Comparative study of compressive strength dependence on the time of hardening (7–180 days) of composite samples based on unmodified and chemically modified hemp hurds showed that chemical treatment of hemp hurds slices did not lead to improvement of mechanical properties of composites. Cause of this phenomenon can be in a nature of used binder and surface properties of modified filler which led to the poor interaction of binder particles and hemp hurds slices. The compressive strength values of composites with modified hemp hurds were ranged from 1.05 to 2.75 MPa in dependence on the hardening time and the values of density were varied from 1065 to 1230 $kg.m^{-3}$. Small differences in compressive strength were found in composites with NaOH treated hemp hurds and hydrated lime.

The favourable values of thermal conductivity coefficient (0.058-0.072 $W.m^{-1}.K^{-1}$) in a relatively narrow range of density values (1100-1185 $kg.m^{-3}$) were measured for composites with hemp hurds treated in NaOH.

Study of durability of 28 days hardened composites based on untreated and chemically modified hemp hurds during their long term water storage confirmed that the surface treatment of hemp hurds slices affects the water absorption behaviour of composites. The most significant changes in sorption behaviour of composites were observed on a specimen with alkaline modified hemp hurds by NaOH. The lowest maximum value of water absorbability was found what is related to the changes in the chemical composition of hemp hurds and in the degradation of degree cellulose polymerization.

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References

[1] L.G. Angelini, A. Lazzeri, G. Levita, D. Fontanelli,C. Bozzi, Ramie (Boehmeria nivea (L.) Gaud.) and Spanish Broom (Spartium junceum L.) “Fibres for composite materials: agronomical aspects, morphology and mechanical properties”, *Ind. Crops Prod,* vol. 11, 2000, pp. 145–161.

[2] H. Savastano, Jr., S.F. Santos, M. Radonjic, W.O. Soboyejo, “ Fracture and fatigue of natural fiber-reinforced cementitious composites”, *Cement Concrete Compos,* vol. 31, 2009, pp. 232–243.

[3] S. Elfordy, F. Lucas, F. Tancret, Y. Scudeller, L. Goudet, “Mechanical and thermal properties of lime and hemp concrete (‘‘hempcrete’’) manufactured by a projection process”, in *Construction and Building Material,*. vol. 22, 2008, pp. 2116–2123.

[4] P.B. de Bruijn, K.H. Jeppssona, K. Sandinb, Ch. Nilssona, “ Mechanical properties of lime–hemp concrete containing shives and fibres”, Biosystems Engineering, vol. 103, 2009, pp. 474-479.

[5] A.B. Thomsen, S. Rasmussen, V. Bohn, K. Nielsen, A. Thygesen, “Hemp raw materials: The effect of cultivar, growth conditions and pretreatment on the chemical composition of the fibres”, *Risø National Laboratory Roskilde*, Denmark, 2005.

[6] E. Gumuskaya, M. Usta, M. Balaban, “Carbohydrate components and crystalline structure of organosolv hemp (Cannabis sativa L.) bast fibers pulp”, *Bioresource Technology*. vol. 98, 2007, pp. 491–497.

[7] M. Karus, D. Vogt, “European hemp industry: cultivation, processing and product lines”, *Euphytica* 140, pp. 7-12.

[8] N.Z. Azwa, B.F. Yousif, A.C. Manalo, W. Karunasena, “A review on the degradability of polymeric composites based on natural fibres”, in *Materials and Design*, vol. 47, 2013, pp. 424-442.

[9] L. Kidalova, N. Stevulova, E. Terpakova, A. Sicakova, “Utilization of alternative materials in lightweight composites”, in *Journal of Cleaner Production*, vol. 34, 2012, pp. 116-119.

[10] E, Terpakova , L. Kidalova, A. Estokova, J. Cigasova, N. Stevulova, “Chemical modification of hemp shives and their characterization”, Procedia Engineering, vol. 42, 2012, pp. 1017-1028.

[11] L. Kidalova, “Determination of selected characteristics in hemp concrete”, Young Scientist: 3rd PhD. Student Conference of Civil Engineering and Architecture, Slovakia, 2011, pp. 1-6.

[12] N. Sombastsompop, K. Chaochanchikul, "Effect of moisture content on mechanical properties, thermal and structural stability and extruded texture of poly(vinylchloride)/wood sawdust composites", in *Polymer International*, vol. 53, 2004, pp. 1210-1218.
[13] STN EN 12390-7, Testing hardened concrete, Part 7, Density of hardened concrete, 2011.
[14] STN EN 12087/A1, Thermal insulating products for building applications, Determination of long term water absorption by immersion, 2007.
[15] J. Cigasova, "Study of chemical changes in modified hemp hurds", Juniorstav 2013: Proc. of 15 th Conference of PhD students. Brno: TU, 2013, pp. 1-7.
[16] J. Cigasova, N. Stevulova, J. Junak, "Influence of binder nature on properties of lightweight composites based on hemp hurds", *International Journal of Modern Manufacturing Technologies,* vol. 5, 2013, no. 2, pp. 27-31.
[17] J. Cigasova, N. Stevulova, A. Sicakova, J. Junak, "Some aspects of lightweight composites durability", in *Chemical Engineering Transactions*, vol. 32, 2013, pp.1615-1620.
[18] J. Cigasova, N. Stevulova, J. Junak, "Innovative use of biomass based on technical hemp in building industry", in *Chemical Engineering Transactions*, vol. 37, 2014, (in press).
[19] N. Stevulova, J. Cigasova, P. Purcz, I. Schwarzova, "Long-term absorption behaviour of hemp hurds composites", in *Chemical Engineering Transactions*. vol. 39, 2014, (in press).
[20] N. Stevulova, J. Cigasova, E. Terpakova, J. Junak, A. Sicakova, A. Estokova, I. Schwarzova, "Chemically modified hemp hurds and testing the properties of composites", Proc. of scientific papers of Institute of Environmental Engineering. Kosice: TU, 2013, pp. 125-137.