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Long-Term Water Absorption Behaviour of Hemp Hurds Composites

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The technical hemp as fast-growing plant belonging to rapidly renewable sources has prospect not only in terms of biomass energy recovery, but also of material in building application in accordance with the principles of sustainable development. Recently, hemp based composites have attracted attention due to their environmentally friendly properties. Because of the main disadvantage of natural plant fibres reinforced composites consisting in high moisture absorption ability of organic filler, chemical treatments of fibres are applied. Moisture in humid atmosphere and water immersion of biocomposites lead to the degradation of fibre-matrix interface as well as mechanical properties.
In this paper, the study of long-term water storage of hemp hurds composites at room temperature was made. Water absorption of composites based on unmodified and chemically modified hemp hurds in dependence on water storage duration was monitored and kinetic curves were described by model. Based on evaluation of sorption curves using model for composites based on natural fibres, diffusion of water molecules in composite is anomalous in terms of the Fickian behaviour.

1. Introduction

One of the possible ways of achievement of sustainable development in the construction 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 great importance to technical hemp like a quickly renewable source of cellulosic fibres with potential for polymer reinforcement of composite and non-waste material is attached in recent years (Preikss et al., 2013). Our study of the properties of 28 d hardened composites based on cellulosic fibers originating from unbleached and bleached pulp (Kidalova et al., 2014) and hemp hurds with inorganic conventional and alternative binders (Kidalova et al., 2012) has shown that physical and mechanical properties of cement/pulp and hemp hurds composites depended on the mean particle length and percentage of filler as well as on used binder. However, low water resistance of these composites was found. Water absorption increased up to 42.5 % after 1 h of immersion of composites in water. Changes of water content in hardened hemp composites (28 – 180 d) are dependent on density of specimens and related to the structural heterogeneity of composites based on porous hemp hurds (Cigasova et al., 2014). Some aspects of lightweight composites durability after their long term storage in deionised water as well as water uptake influence on physical and mechanical properties of composites based on original hemp hurds were studied (Cigasova et al., 2013). Water content in specimens increases with an increasing time of their immersion in water.
Hemp is able to absorb large amounts of water (up to five times its own weight) due to its highly porous structure and strong capillarity effects inside the tubes. Hemp has an ability to regulate humidity inside buildings by absorbing and/or releasing water depending on air conditions (Elfordy et al., 2008).
In humid atmosphere and after long term water immersion of composites based on cellulosic fibres with polymer matrix, the degradation of fibre-matrix interface as well as reduction in mechanical properties of composites was found. The tensile and flexural properties of hemp fiber reinforced unsaturated polyester composites were found to decrease with increase in percentage moisture uptake (Dhakal et al., 2007). The water absorption characteristics for hemp fibers-reinforced unsaturated polyester composites immersed in water at room and elevated temperature were compared in paper (Chen et al., 2013). Effects of water

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absorption on the flexural properties of kenaf fiber unsaturated polyester composites were significantly reduced with incorporation of recycled jute in composites formulation (Osman et al., 2012). Because of this main disadvantage of natural plant fibers reinforced composites consisting in high moisture absorption ability of organic filler, chemical treatments of fibers surface are applied (Faruk et al., 2012). Chemical treatments of fibres and/or polymer and inorganic matrix were performed to improve the interfacial adhesion between fibres and matrix (Kabir et al., 2012). To understand the behaviour of chemically treated hemp fibres, the changes in structure, chemical composition and thermal properties of chemically modified hemp (Cannabis sativa) hurds were investigated by using various methods in comparison with unmodified hemp in our previous paper (Terpakova et al., 2012).

The different physical and mechanical properties of hemp composites based on chemically modified fibers with MgO-cement as an alternative binder were observed in dependence on the character of reagent used for chemical treatment of hemp shives (Stevulova et al., 2012). Short term water immersion of 28-days hardened composites led to higher water absorbability and compressive strength values in comparison to composite with untreated hemp hurds (Stevulova et al., 2013). Hemp fiber treatment with coupling agents caused decrease in water uptake of hemp/fiber/polyethylene composites but also decreased the flexural strength after water exposure (Fang et al., 2013).

Different models have been developed in order to describe the moisture (Wang et al., 2006) and water behavior of natural fiber composites (Sreekala et al., 2003). Diffusion behaviour of composites with polymer matrix can be related to either Fickian, non-Fickian or an intermediate behaviour (Dhakal et al., 2007).

The objective of this work is comparative study of water behaviour of composites based on unmodified and chemically modified hemp hurds in dependence on water storage duration at room temperature. For description of kinetic curves was used model published for sorption behaviour of hemp fibre reinforced unsaturated polyester composites.

2. Material and methods

2.1 Materials

The technical hemp hurds slices (the Netherlands company Hempflax) with polydispersive distribution of particle size were used as the reinforcement in experimental composites. This material consisted of a large majority of woody fibres in the hemp hurds than hemp bast fibres. Chemical composition of used hemp hurds is shown in Table 1. The average moisture content of hemp material determined by weighing of hemp sample before and after drying for 24 h at 105 °C was found 10.78 wt. %.

Table 1: Content of components in hemp hurds

Chemical composition of hemp hurds [%]					
Toluene-ethanol extract	Holocellulose	Cellulose	Hemicellulose	Lignin	Ash
3.5	74.5	44.2	30.3	24.4	1.4

The inorganic matrix in this study was based on so called MgO-cement consisting of the milled calcined MgO (SMZ a.s. Jelsava, Slovakia), silica sand (Sastin, Slovakia) and sodium hydrogen carbonate (p.a).

2.2 Chemical modification of hemp hurds

Chemical treatment of hemp hurds slices was carried out in three chemical environments: in a saturated solution of ethylenediaminetetraacetic acid (EDTA), calcium hydroxide and in solution of sodium hydroxide (Table 2).

Table 2: Used chemicals for modification of hemp hurds

Chemicals	Formula	Producer	Purity
Ethylenediaminetetraacetic acid	$C_{10}H_{16}O_8N_2$	GAVAX s. r. o., Slovakia	p.a.
Calcium hydroxide	$Ca(OH)_2$	ROTH, Germany	≥ 96 %
Sodium hydroxide	NaOH	CHEMAPOL, Slovakia	p.a.

Conditions of chemical modification of the dried hemp hurds were chosen following the literature data (Le Troëdec et al., 2008) and are summarized in Table 3. After chemical treatment fibres were washed with water until the pH value was 7. All prepared samples were then dried in an oven at 70 ºC until a constant weight.

Table 3: Conditions of chemical modification of hemp hurds

Solution	Concentration	Treatment time [h]	Neutralization
EDTA	5 g/L	3	-
$Ca(OH)_2$	2.10^{-2} M	48	-
NaOH	1.6 M	48	1 vol. % acetic acid

2.3 Method of characterization of degree of cellulose polymerization in hemp hurds

The average length of cellulose chains in hemp hurds expressed as average degree of polymerization was determined by using of the method of gel permeation chromatography (Kacik et al, 2009).

2.4 Preparation of composites

Experimental mixtures consisted of 40 vol. % of hemp hurds, 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 in concrete mixer at a speed of 120 rpm for 5 min. Standard steel cube forms with dimensions 100 mm x 100 mm x 100 mm were used for preparation of bodies. The specimens of lightweight composites were cured for 2 days in an indoor climate and then removed from the forms. Curing was continued under laboratory conditions during 28 days. Finally, all hardened composites were dried in a laboratory oven at temperature of 70 °C to constant weight (Cigasova et al., 2013).

2.5 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. After immersion, the specimens were taken out from water and water from all surfaces of bodies has been removed by a clean dry cloth. The specimens were reweighed after long term storage (1 h up to 180 d). 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 represented by (Sombastsompop and Chaochanchikul, 2004) was used to description of sorption curves for composites based on natural fibre (Eq. 1).

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

where M_t, M_∞, are water content at time t and at equilibrium; *k* and *n* are constants giving some information about mechanism of diffusion taking place inside composites. Both 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 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. This fact enables then to find the asymptotic line of the corresponding process of absorption also using the above mentioned method of regression analysis.

3. Results and discussion

Sorption behaviour of hemp composites in water at room temperature is the results of several diffusion processes. Based on the mechanism of water absorption into the composite based on non-treated hemp hurds (Cigasova et al., 2013), the first process is associated with the diffusion of water molecules through the pores on the surface of specimen into micro gaps inside inorganic matrix. Then molecules are capillary transported into the gaps and flaws at the interfaces between hemp hurds slices and the matrix during immersion of composites in water. Further water molecules penetrate into hemp structure, mainly into capillaries and spaces between bundles of fibres and fibrils as well as into hurds spaces. The cellulose structure can be destroyed by penetration of water molecules into the cellulose network of the fibres. The initial absorption stage results in poor wetting and water impregnation of hemp material. High amount of water causes swelling of the fibres. Due to the swelling of the hemp material, microcracking in the matrix of tested composites occurs. These microcracks can be filled with water. However, it is not only water absorption important but also the rate at which the sorption as well as desorption of water molecules takes place (Bruijn et al., 2009). Another phenomenon of water sorption of composites with alternative binder of MgO-cement is connected with the additional hydration of MgO-particles during water storage of

composite. On the other hand there is dissolution of alkaline component in the matrix ($NaHCO_3$), leading to increased pH values of solution up to 12 (Cigasova et al., 2013).
In Figure 1, the water absorption curves of composites based on non-modified and chemically treated hemp hurds slices during long term water storage at room temperature are compared. The water content increases with prolonged time of immersion up to time when water uptake tends to maximum value related to saturation point. Water absorption kinetics of hemp hurds composites were analysed according to the Eq(1). In Table 4, the calculated values of M_∞ and constants k and n for all composites are summarized.

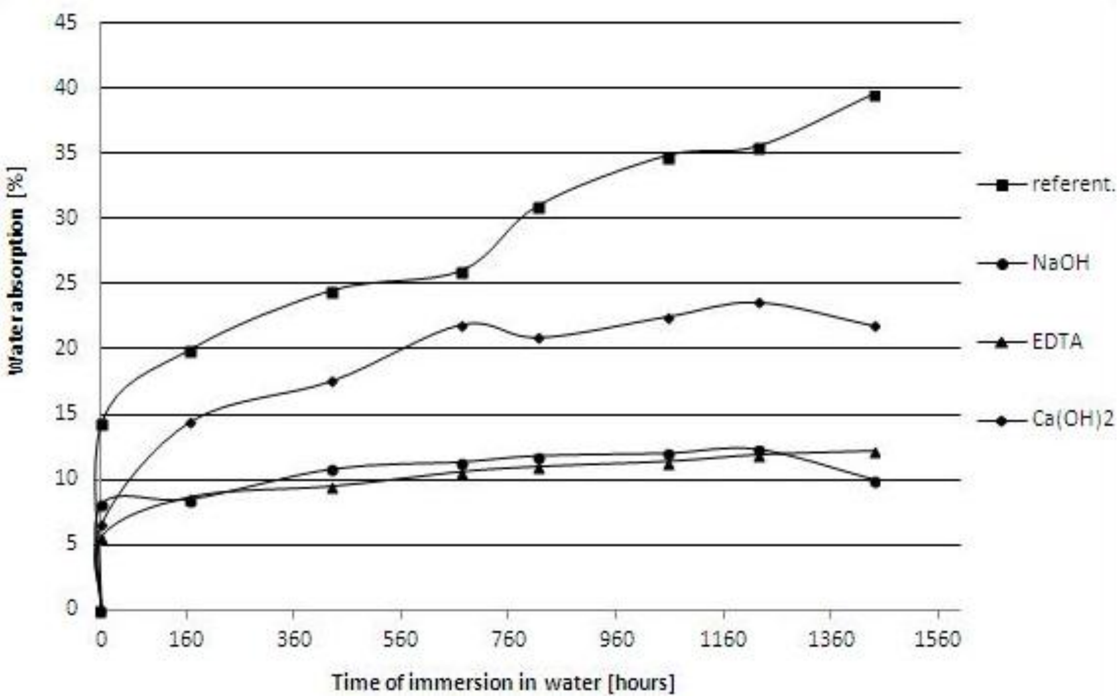

Figure 1: Dependence of water content in composites based on chemically treated hemp hurds on time of their immersion in water

Table 4: Water sorption parameter M_∞, constants k and n calculated from formula (1) for kinetics of long term storage of composites based on chemically modified hemp hurds in comparison to referential composite

Composite	M_∞ [%]	n	k	Correlation coefficient
Referential	45.16	0.1411	0.2765	0.8994
Modified by EDTA	13.26	0.0516	0.6299	0.7824
Modified by $Ca(OH)_2$	27.94	0.1734	0.2331	0.9897
Modified by NaOH	12.81	0.1019	0.4160	0.9814

Surface treatment of hemp hurds slices affects the water absorption rate of composites. The highest saturation water content is observed for referential composite with original hemp hurds. Kinetic of sorption and the maximum value of water absorbability (M_∞) of composites are influenced by the nature of 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 $\approx$ NaOH. Good correlation was found, as indicated by the values of correlation coefficients.
In accordance with literature (Chen et al., 2013), the values of coefficient n indicate the different sorption behaviour of composites based on hemp fibers-reinforced unsaturated polyester composites. It is evident that the water absorption process takes place by diffusion when n = 0.5 following Fickian behavior. For non-Fickian diffusion, the value of n is between 0.5 and 1. When the value of n is less than 0.5, the anomalous diffusion takes place. In the case of hemp hurds composites with inorganic matrix, the values

of *n* calculated from kinetics of water sorption of composites based on unmodified and chemically modified hemp hurds are under 0.5. It means that penetration mobility is much greater than the other relaxation processes. This diffusion is characterized by the development of a boundary between the swollen outer parts of hemp hurds slices and the inner spaces between bundles of fibers and fibrils.
Sorption behavior of composites based on chemically modified hemp hurds slices is related to the surface treatment of organic filler which led to a change in the chemical composition of hemp hurds, but especially in the degradation degree of polymerization of cellulose as shown in Table 5. The most significant changes in the contents of major components in hemp hurds 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.

Table 5: Change in content of main components and average polymerization degree of cellulose (APD) in samples of hemp hurds before and after chemical modification

Chemicals	Cellulose [%]	Hemicellulose [%]	Lignin [%]	APD
Original	44.50	32.78	21.30	1302
EDTA	45.70	31.05	24.22	929
$Ca(OH)_2$	45.75	28.88	23.98	871
NaOH	53.87	12.06	27.27	585

It is interesting that linear dependence between the maximum value of water content in composites and average degree of cellulose polymerization was found ($r = 0.8533$).

4. Conclusions

Sustainable building materials are based on incorporation of renewable natural materials into composites. Benefit of biocomposites with inorganic binders with an elevated pH is inhibition of biological degradation and relevant fire safety. However durability of cellulose based materials is not satisfactory because of their low water absorption resistance. In order to become hemp hurds composite a real material usable in building industry, study of chemical treatment of organic filler in three reagents was carried out in this paper. The comparative study of water absorption behavior of both composites based on unmodified and chemically modified hemp hurds during their long-term storage in deionised water has been shown that surface treatment of filler influenced water sorption process. The maximum value of water absorbability of composites decreases in following order of hemp hurds: original $>$ $Ca(OH)_2$ $>$ EDTA $\approx$ NaOH. Based on evaluation of sorption curves using model for composites based on natural fibers, diffusion of water molecules in composite is anomalous in terms of the Fickian behaviour. The most significant decrease in hydrophility of hemp hurds found in case of alkaline modified of hemp hurds by NaOH relates to change in the chemical composition of hemp hurds, especially to decrease in average degree of cellulose polymerization as well as hemicellulose content.

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