Article

Water Absorption Behavior of Hemp Hurds Composites

Nadezda Stevulova [1], Julia Cigasova [1,*], Pavol Purcz [1], Ivana Schwarzova [1], Frantisek Kacik [2] and Anton Geffert [2]

[1] Department of Material Engineering/Institute of Environmental Engineering,
   Faculty of Civil Engineering, Technical University of Kosice, Vysokoskolska 4, Kosice 042 00,
   Slovakia; E-Mails: nadezda.stevulova@tuke.sk (N.S.); pavol.purcz@tuke.sk (P.P.);
   ivana.schwarzova@tuke.sk (I.S.)

[2] Department of Chemistry and Chemical Technologies, Faculty of Wood Sciences and Technology,
   Technical University in Zvolen, T. G. Masaryka 2117/24, Zvolen 960 53, Slovakia;
   E-Mails: kacik@tuzvo.sk (F.K.); geffert@tuzvo.sk (A.G.)

* Author to whom correspondence should be addressed; E-Mail: julia.cigasova@tuke.sk;
   Tel.: +421-55-602-4278.

Academic Editor: Daolun Chen

Abstract: In this paper, water sorption behavior of 28 days hardened composites based on hemp hurds and inorganic binder was studied. Two kinds of absorption tests on dried cube specimens in deionized water bath at laboratory temperature were performed. Short-term (after one hour water immersion) and long-term (up to 180 days) water absorption tests were carried out to study their durability. Short-term water sorption behavior of original hemp hurds composites depends on mean particle length of hemp and on binder nature. The comparative study of long-term water sorption behavior of composites reinforced with original and chemically modified hemp hurds in three reagents confirmed that surface treatment of filler influences sorption process. Based on evaluation of sorption curves using a model for composites based on natural fibers, diffusion of water molecules in composite reinforced with original and chemically modified hemp hurds is anomalous in terms of the Fickian behavior. The most significant decrease in hydrophility of hemp hurds was found in case of hemp hurds modified by NaOH and it relates to change in the chemical composition of hemp hurds, especially to a decrease in average degree of cellulose polymerization as well as hemicellulose content.

Keywords: hemp hurds; chemical modification; composites; water absorption behavior; sorption kinetics

---

1. Introduction

Bio-based materials are in the foreground of current research in the field of composite. Therefore, over the past years, increasing attention has been devoted to research on composites reinforced with natural fibers. A major aim was to study incorporation of plant fibers as an environmentally friendly, reinforcing agent into composites. Currently, automotive and construction industries have been interested in composites reinforced with natural plant fibers as alternative materials for glass-fiber reinforced composites in structural applications [1].

Composite material based on a polymer matrix reinforced by natural fibers is called in the literature biocomposites. Polymer composites containing different fillers and/or reinforcements are frequently used for automotive application. In recent years, such composites were developed for their application into interior and exterior parts of cars in order to ensure the overall lower weight of the vehicle and increase sustainability of the automotive manufacturing process [2,3].

In response to growing environmental and economic forces, architects, engineers, developers and owners are seeking efficient, innovative building solutions that preserve non-renewable resources. In the building industry, one of the current ways of achievement of sustainable development is to use easily renewable raw material resources and to develop "green concrete". New composites based on natural cellulosic fibers with inorganic matrix (lime) represent a group of lightweight materials providing a healthy living in buildings [4,5].

However, two major factors currently limit the large-scale production of natural fibers composite: poor adhesion between the fiber and matrix and the hydrophilic nature of fibers. A weak adhesion of the matrix acting as a binder with the fibers in composite does not lead to desired mechanical properties in the composite [6]. The hydrophilic nature of fibers is a major problem for their use as reinforcement in polymers. Hydrophilic behavior of plant fibers depends on their composition and specific structure. Low humidity/water resistance of fibers as well as composites reinforced by natural fibers was found [7].

Water sorption in fibers and biocomposites has been found to significantly influence their dimensional and structural properties. Increase in percentage moisture uptake in hemp fiber reinforced unsaturated polyester composites led to decrease in the tensile and flexural properties [8]. The water absorption characteristics for hemp fibers-reinforced unsaturated polyester composites immersed in water at room and elevated temperature were compared in [9]. Effects of water absorption on the flexural properties of kenaf fiber unsaturated polyester composites were significantly reduced with incorporation of recycled jute in composites formulation [10].

Building composites based on the cellulosic fibers like hemp, flax, jute, banana, sisal, pineapple leaf fiber with inorganic matrix (cement, lime, hydraulic lime, gypsum and other alternative binders) are often exposed to humid conditions during their lifetime. Technical hemp, belonging to a great group of plant fibers, is becoming a major focus in terms of its use in green housing because of its health benefit. Its key CO_2-related aspects are avoidance, reuse, mitigation and minimization [11].

The benefit of biocomposites with inorganic binders presenting elevated pH values is inhibition of biological degradation and relevant fire safety. According to [12], hemp has an ability to regulate humidity inside buildings by absorbing and/or releasing water depending on air conditions.

Currently, there is a lack of information on the water absorption behavior of composites reinforced by natural fibers in comparison to biocomposites with polymer matrix. The understanding of the hygroscopic behavior of plant fibers as well as composites reinforced with cellulosic fibers is a key issue in order to use it in different weathering conditions [13] and in order to improve their long-term performance [14]. Therefore, it is important to study in detail the water absorption behavior in order to estimate, not only the consequences that the water absorbed may have, but also the durability of natural fibers composites aged under water.

In order to reduce high moisture/water absorption ability of organic filler in composites, chemical [15–17] or physical treatments of fibers surface are applied [18–20]. Various findings of the water absorbability of composites have been identified. Generally, chemical treatment of natural fibers reduced the overall water uptake of fibers [21] and can positively or negatively affect strength parameters of composites in dependence on plant and matrix kind, treatment conditions of fibrous filler, cellulose content, *etc.* 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 [22].

In our paper [23], some aspects of lightweight composites durability after their long-term storage in deionized water as well as water uptake influence on physical and mechanical properties of composites based on hemp hurds and alternative binder MgO-cement were studied. Water content in specimens increased with increasing time of their immersion in water. Changes in water content after immersion of hardened hemp composites (28–180 days) are dependent on density of specimens and related to the structural heterogeneity of composites based on porous hemp hurds [24]. Sorption behavior of hemp composites in water at room temperature is the result of several diffusion processes. Based on the mechanism of water absorption into the hemp hurds composite [23], 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 fibers 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 fibers. The initial absorption stage results in poor wetting and water impregnation of hemp material. High amount of water causes swelling of the fibers. Due to the swelling of the hemp material, micro cracking in the matrix of tested composites occurs. These micro cracks can be filled with water. However, not only water absorption is important, but also the rate at which the sorption, as well as desorption, of water molecules takes place [25]. Penetrating water molecules are attached onto hydrophilic groups of fibers establishing intermolecular hydrogen bonding with cellulose and degraded interfacial adhesion of fiber/matrix.

Different models have been developed in order to describe the moisture [26] and water behavior of natural fiber composites [27]. Diffusion behavior of composites with polymer matrix can be related to Fickian, non-Fickian or an intermediate behavior [8].

The first objective of this work is to compare the behavior of 28 days hardened composites based on two kinds of hemp hurds, to study the impact of mean particle length of hemp hurds slices and binder

nature after their short-term water immersion. In the second part of this paper, sorption behavior of composites reinforced with original and chemically modified hemp hurds during long-term water storage at room temperature is investigated.

2. Material and Methods

2.1. Material

Hemp Hurds

Two kinds of technical hemp hurds slices (sample 1—Hungarohemp Rt, Nagylak, Hungary; bulk density = 115 kg.m^{-3} and sample 4—Hempflax, Oude Pekela, Netherlands; bulk density = 117.5 kg.m^{-3}) with a wide particle size distribution were used in experiments. Both materials consisted of a large majority of woody fibers from hemp hurds rather than from hemp bast fibers and also contained fine dust particles originating from the manufacturing grinding process. Six samples of hemp hurds (2 original samples and 4 fractions—samples 2, 3, 5, 6) were used as the reinforcement into experimental composites. Mean particle length values of all hemp hurds samples are given in Table 1.

Table 1. Mean particle length, in d$_m$, of hemp hurds samples.

Hemp	Sample	d$_m$ (mm)
Hungarohemp	1	4.29
	2	7.42
	3	2.33
Hempflax	4	1.94
	5	3.22
	6	0.94

As shown in Table 2, original hemp hurds samples are mainly composed on sugar-based polymers (holocellulose: cellulose and hemicelloses) combined with lignin. Additional components, such as waxes or oils (toluene-ethanol extract) and structural water were found. The average moisture content of hemp materials determined by weighing of hemp sample before and after drying for 24 h at 105 °C was 10.13 and 10.78 wt.%. Presence of pectin was confirmed by Fourier Transform Infrared Spectroscopy. Chemical analysis of hemp hurds fractions did not reveal differences in contents of hemp hurds constituents.

Table 2. Chemical composition of hemp hurds slices (original sample).

Hemp hurds component	Content (%)	
	Hungarohemp	Hempflax
Holocellulose	71.5	74.5
Cellulose	44.3	44.2
Hemicellulose	27.2	30.3
Lignin	22.0	24.4
Toluene-ethanol extract	6.2	3.5
Ash	1.6	1.4

The inorganic matrix in this study was based on Portland cement CEM I 42.5 R (classical binder component) and 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). Fine dispersed product of MgO was obtained by short-term dry milling (5 min) in laboratory vibratory mill VM 4 [28].

2.2. Methods

2.2.1. Chemical Modification of Hemp Hurds

The chemical modification of dried hemp hurds was made by three different solutions: sodium hydroxide (NaOH) p.a. (CHEMAPOL, Prague, Czech Republic), pulverized calcium hydroxide (Ca(OH)$_2$) with purity $\geq$ 96%) (ROTH, Karlsruhe, Germany), ethylenediamintetracetic acid (EDTA) p.a. (GAVAX s.r.o., Vranov nad Toplou, Slovakia). The specification of the chemical treatment conditions is described in [29].

2.2.2. Determination of Hemp Hurds Components

A milled and oven-dried sample was used for the determination of chemical composition of hemp hurds. Extractives were determined in a Soxhlet apparatus (Kavalier Glass, Sázava, Czech Republic) with a mixture of ethanol and toluene (2:1) for 8 h, according to the American Society for Testing and Materials (ASTM). Total content of polysaccharides (*i.e.*, holocellulose) was determined using the method of [30]. Cellulose content was determined by the Seifert method [31]. A mixture of acetylacetone, dioxane, and hydrochloric acid (6:2:1.5) under reflux for 30 min was used for delignification of samples. The content of hemicelluloses was determined as the difference between holocellulose and cellulose. The content of acid-insoluble (Klason) lignin was determined according to the U.S. Department of Energy, National Renewable Energy Laboratory analytical procedure [32]. The samples were hydrolyzed in a two-stage process. In the first stage, 72% (w/w) H$_2$SO$_4$ at a temperature of 30 °C was used for 2 h, and in the second stage, the samples were refluxed after dilution to 4% (w/w) H$_2$SO$_4$ for 4 h. Total ash content (mineral substances) was determined according to the U.S. Department of Energy, National Renewable Energy Laboratory analytical procedure [33].

2.2.3. Size Exclusion Chromatography

Molecular weight distribution analysis of the cellulose samples was performed by size exclusion chromatography (SEC) after their conversion into tricarbanilates. Cellulose tricarbanilates were dissolved in tetrahydrofuran and filtered through a Puradisc 25 NYL filter (Whatman International, Maidstone, UK) with a pore size of 0.45 μm. SEC was performed at 35 °C with tetrahydrofuran at a flow rate of 1 mL·min^{-1} on two PLgel (porous polystyrene/divinylbenzene matrix with particle size of 10 μm and internal diameter × length of 7.5 × 300 mm) MIXED-B columns (Agilent Technologies, Santa Clara, CA, USA) preceded by a PLgel (10 μm, 7.5 × 50 mm), Guard-column (Agilent Technologies) as described by [34]. Data acquisitions were carried out with ChemStation software (Agilent Technologies, Santa Clara, CA, USA) and calculations were performed with the Clarity GPC module (DataApex, Prague, Czech Republic). Numerical outputs obtained for Mn (number-average molecular weight) and Mw (weight-average molecular weight) were recalculated to underivatized

cellulose by multiplication with the coefficient k = 162/519. Polydispersity index (PDI) of cellulose was calculated as the ratio Mw/Mn. Degree of polymerization (DP) values were calculated by dividing the molecular weight by the monomer equivalent weight of anhydroglucose (DPw = M/162).

2.2.4. Fresh Mixture and Composite Preparation

Experimental mixtures were prepared according to the recipe and consisted of 40 vol.% of filler (unmodified hemp hurds as referential material—samples 1 and 4; hemp hurds fractions—samples 2, 3, 5 and 6; chemically treated samples), 29 vol.% of binder 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 × 100 mm × 100 mm 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 for 28 days.

2.2.5. Water Absorption Tests

Two kinds of absorption tests on dried cube specimens of hemp hurds composites after 28 days of hardening in deionized water bath (PE closed container) at laboratory temperature (23 °C) were performed. Short-term water absorption test (after one hour immersion) was made according to Slovak standard (STN EN 12087/1). Long-term water absorption was conducted by immersing the specimens for different time durations (up to 180 days) to study their durability. After immersion for given time, the specimens were taken out from the water and water from all surfaces of bodies was removed by a clean dry cloth. All specimens were weighted again after their storage. 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. The water absorption kinetic model [35] was used to describe the sorption curves for composites based on natural fiber (1):

$$\frac{M_t}{M_\infty} = \mathrm{k}t^{\mathrm{n}}$$

(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. 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 are 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.

The diffusion properties composites represent the ability of the water molecules moving inside the specimens were evaluated by the coefficient of diffusion D according to the following formula [36]:

$$\mathrm{D} = \pi(kh/4\mathrm{M}_\infty)^2$$

(2)

where *k* is the slope of the linear part of water absorption curve and *h* is the initial thickness of the composites.

3. Results and Discussion

Studying the water absorption behavior of the biocomposites is very important because of poor water resistance of fibrous biomaterial. In building application, mainly for outdoor use of biocomposites, water absorbability is one of the most important parameters impacting their mechanical properties and dimensional stability. The study of water sorption and thickness swelling of natural fibers plastic composites [10,37,38] confirmed that this behavior of composites with a given fiber content depends on a wide array of factors, including fiber/matrix interface quality, chemical composition and length of fibers, their distribution in composite, permeability nature and porosity of fibers and density. Recently, a limited focus on the analysis of the water sorption properties of fibers and inorganic matrix has been addressed. To contribute to a better understanding of the water sorption process in composites with the same volume fraction of hemp hurds, short- and long-term water storage study of 28 days hardened specimens took place at room temperature.

3.1. Short-Term Water Absorption Behavior of Composites

The research of short-term water sorption behavior of composites was directed to study the influence of selected constituent parameters such as the mean particle length of hemp hurds and matrix materials on the water uptake of hemp hurds composites. The mean particle length of Hungarian and Dutch hemp hurds on water uptake of composites with these organic fillers and MgO-cement during their short-term storage in water was studied. Figure 1 shows water absorbability of hemp hurds reinforced composites as a function of mean particle length of filler component. Composites based on Hungarian hemp hurds samples with longer mean particle length acquired higher values of water content (11.9–25.8 wt.%) while in Dutch plant composites lower water absorbability values were observed (6.3–14.3 wt.%). Water content values in immersed composites based on Hungarian hemp hurds increase with increasing mean particle length but composites with Dutch filler behave differently. In this case, water absorbability of composites first increases and then decreases with increasing mean particle length of hemp hurds. The hydrophilic behavior of plant fibers is mainly due to two factors: their composition and their specific structure. As is evident from Table 2, this different behavior of composites based on the Dutch hemp hurds most likely cannot be caused by the chemical composition of filler. The high level of water absorption in hemp hurds is determined by their particular structure. The hemp hurds layered structure forming by fibrils, microfibrils and fibers is porous and has a high exchange surface. At the scale of cellulose microfibrils, transport of water molecules could take place in the amorphous region where hydrophilic polymers are present (hemicellulose and lignin). The effect of extremely complicated microstructure of hemp hurds, its heterogeneity of the properties due to fiber separation procedure has to be taken into account at water sorption behavior of these composites. The differences in porosity of hemp hurds slices in composite could be considered as a further possible reason for explanation of short-term water sorption behavior of samples 4–6. However, currently, the porosity content in hemp hurds is unknown.
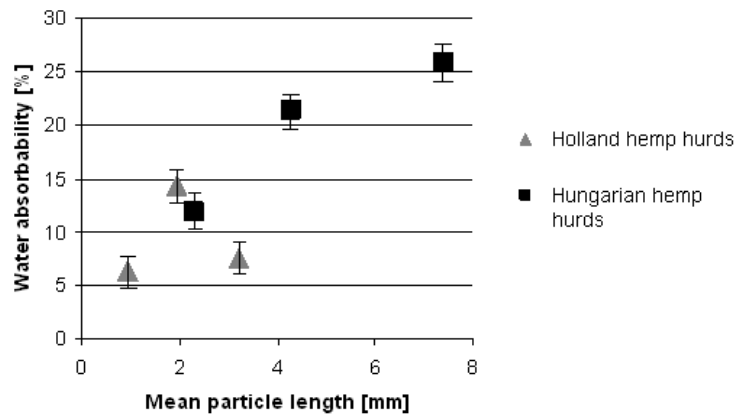
Figure 1. Water absorption depending on mean particle length of composites based on two types of hemp hurds.

An inhomogeneous local distribution of two components in hemp hurds slices volume and on surfaces of particles: hemicellulose as the most hydrophilic component in hemp hurds and lignin providing the water molecules transport could be responsible for different water content in these composites. It is known that hemp in particular shows inhomogeneous properties within the stalk lengths, which are dependent on the growing conditions [15]. One of the most important factors controlling the water diffusion in polymeric materials is the molecular interaction occurring between the diffusing compound and the substrate [13]. The water sorption during short-term water immersion of the composite could occur at specific sites (polar groups of hemp hurds components) by hydrogen bonding. Finally, differential behavior of composites during their short-term storage is determined by the complex of possible causes including the swelling of the fibrous material.

Based on the comparative study of the measured water absorbability values of 28 days hardened composites with hemp hurds of different mean particle length after their short-term water immersion, Dutch hemp hurds composites (with shorter length of slices) were selected for further investigation of binder nature effect on water sorption properties due to their lower water contents. The water absorption values of prepared composite samples are shown in Figure 2. In both types of composites, water uptake is determined by mean particle length of hemp hurds slices as well as by nature of matrix. As shown in Figure 2, water uptakes in hemp hurds composites with Portland cement are 1.9–2.4 times higher than in specimens based on alternative binder MgO-cement. It means the water resistance of MgO-cement based composites is higher than the water resistance of cement based materials. This fact could be related to the higher degree of porosity of hemp hurds cement-based composites caused by ongoing hydration processes. Composites with higher porosity also have more poor compactibility between organic filler and cement mixture.

3.2. Long-Term Water Absorption Behavior of Composites

MgO-cement based composites with original (non-modified) and chemically treated hemp hurds slices (Hempflax) after 28 days of hardening were subjected to long-term immersion in water. In Figure 3, the water absorption curves of these composites during long-term water storage at room temperature are compared. The water content increases with prolonged time of immersion up to the time when water uptake tends to the maximum value related to saturation point. The water sorption at

room temperature takes far longer period to reach saturation equilibrium. Water absorption kinetics of hemp hurds composites were analyzed according to Equation (1). In Table 3, the calculated values of $M\infty$, constants k, n and D for all composites are summarized. As Figure 3 and Table 3 show, surface treatment of hemp hurds slices has a positive impact on the water absorption behavior of composites. The highest saturation water content is observed for reference composites with original hemp hurds. Kinetic of sorption and the maximum value of water absorbability (M_∞) of composites are influenced by the nature of hemp hurds surface. It is evident that chemical modification of hemp hurds reduced the water uptake of the resulting composites. The following order of composites based on original and chemically modified hemp hurds in terms of the maximum value of $M\infty$ was found:

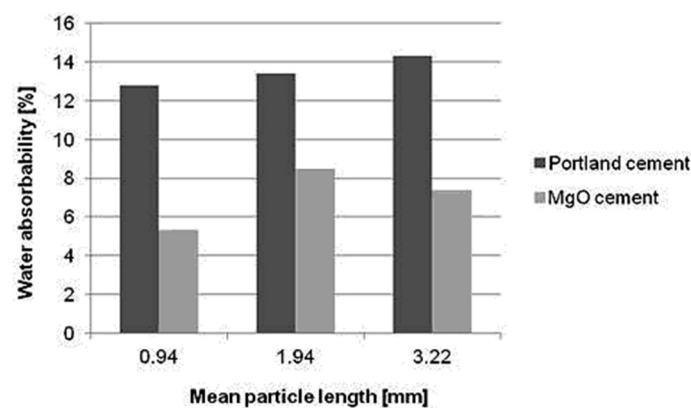$$\text{reference} > Ca(OH)_2 > EDTA \approx NaOH \tag{3}$$

Figure 2. Water absorption depending on mean particle length of composites based on Dutch hemp hurds and two types of binders.
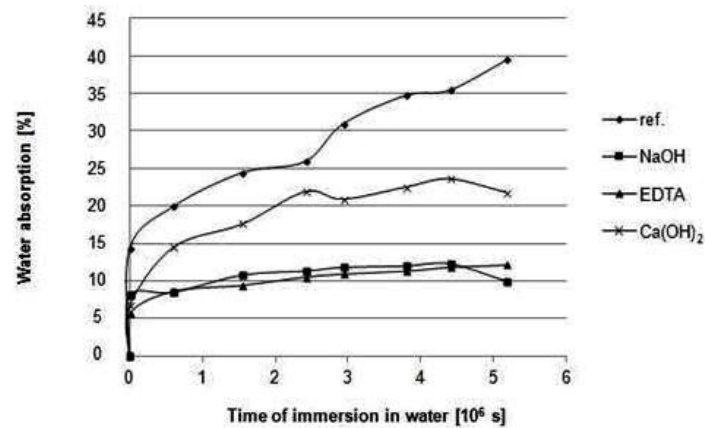

Figure 3. Dependence of water absorption of composites on the time of their immersion in water.

Table 3. Diffusion parameter of composites based on chemically modified hemp hurds in comparison to reference composite.

Composites samples	M_∞ (%)	n	k (s^{-1})	Correlation coefficient	D ($m^2.s^{-1}$)
Reference	45.16	0.1411	7.68×10^{-5}	0.8994	0.058×10^{-11}
Modified by EDTA	13.26	0.0516	17.50×10^{-5}	0.7824	3.42×10^{-11}
Modified by Ca(OH)$_2$	27.94	0.1734	6.48×10^{-5}	0.9897	0.106×10^{-11}
Modified by NaOH	12.81	0.1019	11.56×10^{-5}	0.9814	1.66×10^{-11}

Good correlation between experimental and model kinetics was found, as indicated by the values of correlation coefficients. The values of calculated correlation coefficients for the water absorption curves of all composites are higher than the critical value of the correlation coefficient (0.664) for a set of measured values at elected significance level p = 0.05. The existence of a relationship between variables such as water content and time of water immersion of composite at given significance level can be regarded as proven.

As can be seen in Table 3, the values of coefficient n indicate the different sorption behavior of composites reinforced by hemp hurds. According to the evaluation of water sorption curves of hemp fiber reinforced unsaturated polyester composites [8,9], 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, 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 affected 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. This is reflected in the diffusion coefficients values. Table 3 shows higher values of diffusion coefficients of composites with modified hemp hurds in comparison to reference composite. Thus, the ability of water molecules to move inside hemp composite is accelerated by incorporation of modified fibers. The mechanisms describing the transport of water in fibrous composites are still not perfect. There is needed to consider both effect of diffusion and capillarity.

The reduced hydrophility of hemp hurds is one of the reasons for the decreasing water uptake of composites based on chemically modified hemp hurds. The results obtained at study of treatment of hemp hurds with NaOH, EDTA and $Ca(OH)_2$ are in accordance with data in [39]. Partial removal of amorphous compounds mainly hemicelluloses from the surface of fibers bundles by NaOH treatment was found, EDTA treatment led to separation fibers and calcium ions associated with pectin and lime hydroxide treatment involved a fixation of Ca^{2+} ions at the surface of fibers [40]. NaOH treatment is used to decrease the hydrogen bonding capacity of cellulose; it reacts with the hydroxyl groups present in cellulose to form water molecules. In this way, the number of hydroxyl groups tending to bond with water molecules is decreasing [39].

Sorption behavior of composites based on chemically modified hemp hurds slices is related to the change in chemical composition of hemp hurds, as shown in [40], but especially in the degradation degree of polymerization of cellulose (Table 4). The most significant changes in the contents of cellulose, hemicellulose and lignin in hemp hurds and in average degree of cellulose polymerization were recorded in NaOH modified hemp hurds. Based on knowledge of the water absorption in the cellulose structure [13], water absorbability of treated samples is related to crystallinity degree of the cellulose. The water content decreases in the cellulose as the crystallinity degree of the cellulose increases in chemically treated hemp hurds samples [40]. Amorphous component such as hemicellulose plays also an important role in the water storage. Fibers with higher hemicellulose content absorb more moisture [38]. Significantly lower water content was observed in hemp fibers after partial removal of hemicelluloses and lignin [41], reducing the ability of fibers to absorb water.

Table 4. Changes in content of main components and average polymerization degree of cellulose (APD) in samples of hemp hurds before and after chemical modification.

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

Linear dependence between the maximum value of water content in composites and average degree of cellulose polymerization was found (r = 0.8533) [42]. Figure 4 shows relationship between value of M_∞ of composites and content of hemicelluloses in hemp hurds samples. This fact is in accordance with data mentioned above.
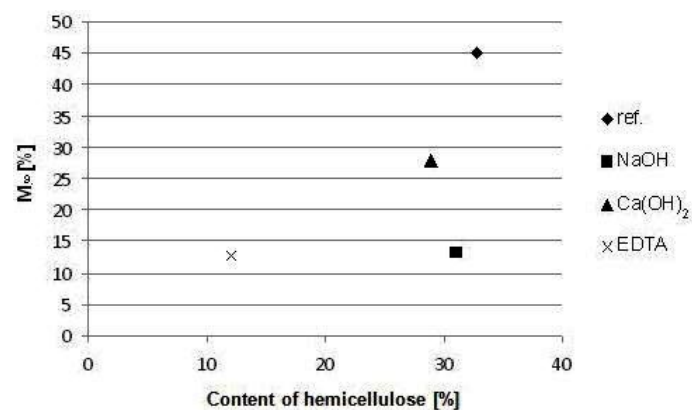
Figure 4. Dependence of water sorption parameter M_∞ on hemicellulose content in hemp hurds samples.

4. Conclusions

Durability of cellulose-based materials (such as hemp hurds) is not satisfactory because of their low water absorption resistance. In order to become hemp hurds composite as real material usable in building industry, water sorption behavior of 28 days hardened composites based on hemp hurds and inorganic binder was studied during their short- and long-term storage at room temperature. This includes the investigation of the impact of kinds, mean particle length and chemical modification of hemp hurds as well as binder nature on water absorbability of composites. The results can be summarized as follows:

4.1. Short-Term Water Absorption Behavior

1. Testing of water absorption behavior of original hemp hurds composites with classical (Portland cement) and alternative binder (MgO-cement) showed that the more suitable binder for lightweight composite is MgO-cement. Its alkaline nature positively affects surface of filler as well as its interaction with hemp hurds.
2. According to the results, decreasing mean particle length positively influences water absorbability of composites.

3. Lower water contents in composites reinforced with Dutch hemp hurds (shorter particle length) and MgO-cement were recorded in comparison to composites with Hungarian hemp hurds.

4.2. Long-Term Water Absorption Behavior

1. The degree of water absorption in hemp hurds composites depends on their duration of water immersion.
2. The comparative study of water sorption behavior of composites reinforced with original and chemically modified hemp hurds in three reagents confirmed that surface treatment of filler influences of sorption process. The maximum value of water absorbability of composites decreases in following order of hemp hurds: original > $Ca(OH)_2$ > EDTA ≈ NaOH.
3. Based on evaluation of sorption curves using model for composites based on natural fibers, diffusion of water molecules in composite reinforced with original and chemically modified hemp hurds is anomalous in terms of the Fickian behavior.
4. 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.

Acknowledgments

Author Contributions

Nadezda Stevulova: (1) initiated the overall research concept and supervised the research work of Julia Cigasova; (2) completed the initial manuscript; (3) revised critically the content of the paper. Julia Cigasova: (1) carried out experiments of hemp hurds characterization, chemical modification and water absorbability. Pavol Purcz: (1) calculation of mathematical statistical data. Ivana Schwarzova: (1) prepared the initial manuscript; (2) analyzed data and partially interpreted. Changes in chemical composition of samples were determined by Anton Geffert. Frantisek Kacik: (1) performed and interpreted SEC measurements; (2) contributed to manuscript writing.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Saikia, D. Investigations on structural characteristics, thermal stability, and hygroscopicity of sisal fibers at elevated temperatures. *Int. J. Thermophys.* **2008**, *29*, 2215–2225.
2. Holbery, J.; Houston, D. Natural-fiber-reinforced polymer composites in automotive application. *JOM* **2006**, *11*, 80–86.

3. Bledzki, A.K.; Faruk, O.; Sperber, V.E. Car from bio-fibres. *Macromol. Mater. Eng.* **2006**, *291*, 449–457.

4. Le Troëdec, M.; Dalmay, P.; Patapy, C.; Peyratout, C.; Smith, C.; Chotard, D. Mechanical properties of hemp-lime reinforced mortars: influence of the chemical treatments of fibers. *J. Compos. Mater.* **2011**, *45*, 2347–2357.

5. Preikss, I.; Skujans, J.; Adamovics, A.; Iljins, U. Evaluation of hemp (Cannabis Sativa L.) quality parameters for building materials from foam gypsum products. *Chem. Eng. Trans.* **2013**, *32*, 1639–1644.

6. Srinivasa, C.V.; Suresh, Y.J.; Premakumar, W.P. Mechanical behavior of areca fiber reinforced epoxy composites. *Adv. Polym. Technol.* **2011**, *31*, 319–330.

7. Célino, A.; Fréor, S.; Jacquemin, F.; Casari, P. Characterization and modeling of the moisture diffusion behaviour of narural fibres. *J. Appl. Polym. Sci.* **2013**, *130*, 297–306.

8. Dhakal, H.N.; Zhang, Z.Y.; Richardson, M.O.W. Effect of water absorption on the mechanical properties of hemp fibre reinforced unsaturated polyester composites. *Comp. Sci. Technol.* **2007**, *67*, 1674–1683.

9. Chen, T.; Liu, W.; Qiu, R. Mechanical properties and water absorption of hemp fibers-reinforced unsaturated polyester composites: Effect of fiber surface treatment with heterofunctional monomer. *BioResource* **2013**, *8*, 2780–2791.

10. Osman, E.A.; Vakhguelt, A.; Sbarski, I.; Mutasher, S.A. Kenaf/recycled jute natural fibers unsaturated polyestermcomposites: Water absorption/dimensional stability and mechanical properties. *Int. J. Comput. Mater. Sci. Eng.* **2012**, *1*, 1–17.

11. Klemeš, J.; Varbanov, P.S.; Huisingh, D. Recent cleaner production advances in process monitoring and optimization. *J. Clean. Prod.* **2012**, *34*, 1–8.

12. Elfordy, S.; Lucas, F.; Tancret, F.; Scudeller, Y.; Goudet, L. Mechanical and thermal propertis of lime and hemp concrete ("hempcrete") manufactured by a projection process. *Constr. Build. Mater.* **2008**, *22*, 2116–2123.

13. Célino, A.; Fréor, S.; Jacquemin, F.; Casari, P. The hygroscopic behavior of plant fibers: A review. *Front Chem.* **2014**, *43*, 1–12.

14. Saikia, D.; Bora, M.N. Study of hygroscopic properties of some plant fibres under thermal condition. *Indian J. Pure Appl. Phys.* **2003**, *41*, 484–487.

15. Faruk, O.; Bledzki, A.K.; Fink, H.P.; Sain, M. Biocomposites reinforced with natural fibres: 2000–2010. *Prog. Polym. Sci.* **2012**, *37*, 1552–1596.

16. Le Troedec, M.; Peyratout, C.S.; Smith, A.; Chotard, T. Influence of various chemical treatments on the interactions between hemp fibres and a lime matrix. *J. Eur. Ceram. Soc.* **2009**, *29*, 1861–1868.

17. Kabir, M.; Wang, H.; Lau, K.; Cardona, F.; Aravinthan, T. Mechanical properties of chemically-treated hemp fibre reinforced sandwich composites. *Compos. Part B* **2012**, *43*, 159–169.

18. Renouard, S.; Hano, C.; Doussot, J.; Blondeau, J.P.; Lainé, E. Characterization of ultrasonic impact on coir, flax and hemp fibers. *Mater. Lett.* **2014**, *129*, 137–141.

19. Sgriccia, N.; Hawley, M.C. Thermal, morphological and electrical characterization of microwave processed natural fiber composites. *Compos. Sci. Technol.* **2007**, *67*, 1986–1991.

20. Thomsen, A.B.; Thygesen, A.; Bohn, V.; Nielsen, K.V.; Allesen, B.; Jorgensen, M.S. Effects of chemical and physical pre-treatment processes on hemp fibres for reinforcement of composites and for textiles. *Ind. Crop. Prod.* **2006**, *24*, 113–118.

21. Patel, B.C.; Acharya, S.K.; Mishra, D. Environmental effect of water absorption and flexural strength of red mud filled jute fiber/polymer composite. *Int. J. Eng. Sci. Technol.* **2012**, *4*, 49–59.

22. Fang, H.; Zhang, Y.; Deng, J.; Rodrigue, D. Effect of fiber treatment on the water absorption and mechanical properties of hemp fiber/polyethylene composites. *J. Appl. Polym. Sci.* **2013**, *127*, 942–949.

23. Cigasova, J.; Stevulova, N.; Sicakova, A.; Junak, J. Some aspects of lightweight composites durability. *Chem. Eng. Trans.* **2013**, *32*, 1615–1620.

24. Cigasova, J.; Stevulova, N.; Schwarzova, I.; Junak, J. Innovative use of biomass based on technical hemp in building industry. *Chem. Eng. Trans.* **2014**, *37*, 685–690.

25. Bruijn, P.B.; Jeppson, K.H.; Sandin, K.; Nilson, C. Mechanical properties of lime-hemp concrete containg shives and fibres. *Biosyst. Eng.* **2009**, *103*, 474–479.

26. Wang, W.; Sain, M.; Cooper, P.A. Study of moisture absorption in natural fibre composites. *Compos. Sci. Technol.* **2006**, *66*, 379–386.

27. Sreekala, M.S.; Thomas, S. Effect of fibre surface treatment on water sorption characteristics of oil palm fibres. *Compos. Sci. Technol.* **2003**, *63*, 861–869.

28. Kidalova, L.; Stevulova, N.; Terpakova, E.; Sicakova, A. Utilization of alternative materials in lightweight composites. *J. Clean. Prod.* **2012**, *34*, 116–119.

29. Terpakova, E.; Kidalova, L.; Estokova, A.; Cigasova, J.; Stevulova, N. Chemical modification of hemp shives and their characterization. *Proc. Eng.* **2012**, *42*, 1017–1028.

30. Wise, L.E.; Maxine, M.; D'Addieco, A.A. Chlorite holocellulose, its fractionation and bearing on summative wood analysis and on studies on the hemicelluloses. *Paper Trade J.* **1946**, *122*, 35–43.

31. Seifert, V.K. Über ein neues Verfahren zur Schnellbestimmung der Rein—Cellulose. *Papier* **1956**, *10*, 301–306.

32. Sluiter, A.; Hames, B.; Ruiz, R.; Scarlata, C.; Sluiter, J.; Templeton, D.; Crocker, D. *Determination of Structural Carbohydrates and Lignin in Biomass*; Technical Report NREL/TP-510–42618; National Renewable Energy Laboratory: Golden, CO, USA, 2010.

33. Sluiter, A.; Hames, B.; Ruiz, R.; Scarlata, C.; Sluiter, J.; Templeton, D. *Determination of Ash in Biomass*; Technical Report NREL/TP-510–42622; National Renewable Energy Laboratory: Golden, CO, USA, 2008.

34. Kacik, F.; Kacikova, D.; Jablonsky, M.; Katuscak, S. Cellulose degradation in new-sprint paper ageing. *Polym. Degrad. Stab.* **2009**, *94*, 1509–1514.

35. Sombastsompop, N.; Chaochanchikul, K. Effect of moisture content on mechanical properties, thermal and structural stability and extruded texture of poly(vinylchloride)/wood sawdust composites. *Polymer Int.* **2004**, *53*, 1210–1218.

36. Sreekumar, P.A.; Thomas, S.P.; Saiter, J.M.; Joseph, K.; Unnikrishnan, G.; Thomas, S. Effect of fiber surface modification on the mechanical and water absorption charakteristic of sisal/polyester composites fabricated by resin transfer molding. *Compos. Part A* **2009**, *40*, 1777–1784.

37. Tajvidi, M.; Takemura, A. Recycled natural fiberpropylene composites: Water absorption/ desorption kinetics and dimensional stability. *J. Polym. Environ.* **2010**, *18*, 500–509.

38. Azwa, N.Z.; Yousif, B.F.; Manalo, A.C.; Karusena, W. A review on the degradability of polymer composites based on natural fibres. *Mater. Des*. **2013**, *47*, 424–442.

39. Le Troëdec, M.; Sedan, D.; Peyratout, C.; Bonnet, J.P.; Smith, A.; Guinebretiere, R.; Gloaguen, V.; Krausz, P. Influence of various chemical treatments on the composition and structure of hemp fibres. *Compos. Part A* **2008**, *39*, 514–522.

40. Stevulova, N.; Cigasova, J.; Estokova, A.; Terpakova, E.; Geffert, A.; Kacik, F.; Singovszka, E.; Holub, M. Properties characterization of chemically modified hemp hurds. *Materials* **2014**, *7*, 8131–8150.

41. Pejic, B.M.; Kostic, M.M.; Skundric, P.D.; Praskalo, J.Z. The effects of hemicelluloses and lignin removal on water uptake behaviour of hemp fibres. *Bioresour Technol*. **2008**, *99*, 7152–7159.

42. Stevulova, N.; Schwarzova, I. Changes in the properties of composites caused by chemical treatment of hemp hurds. *Int. J. Chem. Nucl. Metall. Mater. Eng*. **2014**, *8*, 388–392.