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Influence of chemical modification on hemp–starch concrete

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HIGHLIGHTS

- The impact of surface treatments on hemp–starch composite was studied.
- Alkaline treatment removes amorphous compound on hemp hurds surface.
- Silane coupling agent creates a cross-linked network.
- Using alkaline treatment followed by silane coupling agent improve mechanical properties of hemp–starch composite.

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ABSTRACT

As a result of growing environmental consciousness, the issues of sustainability and industrial ecology are guiding the development of the next generation of materials and processes. Renewable resources such as hemp hurds in the field of green polymeric materials with their new range of applications represent an important basis in order to fulfil the ecological objective of creating eco-friendly materials.

This work deals with the impact of several chemical treatments of hemp hurds on the properties of hemp–starch composite which is made of 100% of natural resources. Two compositions were manufactured, the first one with untreated hemp hurds in starch matrix and the second one with treated hemp hurds in starch matrix. A set of chemical treatments was performed to solubilize hemicelluloses and lignin seal surrounding the cellulose bundle in the first step and then a coupling agent was used to provide a stable bond between hemp hurds and starch matrix. The influence of the treatments on hemp hurds characteristics was investigated by scanning electron microscopy (SEM), differential thermal analysis (DTA), thermogravimetric analysis (TGA) and attenuated total reflectance spectroscopy (ATR). Moreover, the mechanical properties of green composites were studied and it seems that alkaline treatment followed by silane treatment improves the stiffness of composites according to the results of mechanical properties after treatments.

1. Introduction

Energy consumption of building sector in France covers 43% of the total energy consumption. The maximum power consumption comes from building heating, which depends on the efficiency of building envelopes. Using vegetal-based materials such as hemp hurds increases the energy efficiency in envelopes due to their porous structure, reduces production cost and relatively the emission of carbon dioxide that causes climatic change and allows the production of lightweight mortars [1,2]. The environmental benefits of hemp-based composites for building thermal insulation, in place of traditional materials such as rock wool, have been quantitatively assessed by life cycle assessment (LCA) [3].

Hemp hurds obtained from hemp plant (cannabis sativa, non-narcotic hemp) in the inner woody part of the stem. Chemical composition of hemp hurds is as follows: cellulose (36–41%), hemicellulose (31–37%), lignin (19–21%), wax (<1%) and minerals (<4%) [4]. Cellulose is semicrystalline polysaccharide made with D-glucopyranose units linked together by β(1–4) glucosidal bond. Hydroxyl group from cellulose are responsible of hydrophilic properties. Hemicellulose have a lower molecular weight than cellulose and amorphous. It is strongly bound to cellulose fibrils by hydrogen bound and has many hydroxyl and acetyl groups. Lignin is amorphous, aromatic and has polymers of phenyl propane units. Each elementary component is a network of ultrafine cellulose fibrils embedded in matrix of hemicellulose and lignin [5].

So far, numerous studies have been performed on composites containing hemp hurds. Hemp hurds are suitable for thermal and acoustic insulating due to their porous structure and they are used

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as reinforcement for building materials based on hydraulic lime, gypsum, and cement binders [6]. The binder is often made with additional components which can modify or improve already existing characteristics such as pozzolanic additives [2].

Physical and mechanical properties of hemp based composites depend on the size and morphology of hemp hurds, matrix properties and hemp/matrix interaction [6]. Therefore, chemical treatments of hemp hurds are considered in modifying surface properties to enhance the adhesion with the polymer matrix and also improve mechanical properties [7,8]. Moreover, several studies on hemp concrete used a mineral matrix mainly lime matrix. The extraction process of mineral matrix contributes to the depletion of natural resources [9] and using a vegetal matrix like starch is ecologically interesting.

Among biopolymers, starch is one of the most promising renewable bio-resources due to competitiveness in price and applicability to various industries. It has been found that using reinforced materials in a starch matrix is an effective method to obtain high performance starch-based bio-composites. Starch is extracted form cereal seeds (wheat, maize, rice), tubers (potato) and roots (tapioca). Chemically, starch is polymeric carbohydrate consisting of glucose units linked together by α(1–4) bonds. It is generally established that starch is a heterogeneous material containing amylose (essentially a linear structure of 1–4 linked glucose units) and amylopectin (highly branched structure of 1–4 short chains linked by 1–6 bonds). The high molecular weight and branched structure of amylopectin reduce the mobility of the polymer chains and interfere with a tendency for them to become oriented closely enough to permit significant levels of hydrogen bonding [10].

A few works are devoted to starch-based composite with hemp hurds. Balčiūnas used unmodified corn starch binder with hemp hurds and evaluate mechanical properties of starch-based composites. He showed that starch granules form a hardened paste that covers the wall of hurds evenly creating a homogeneous structure. A compressive strength of 1913 kPa was found for a density of 480 kg/m^3 compared to 1553 kPa for a cement binder composite with a density of 519 kg/m^3 [4]. Starch matrix reinforced by sisal fibers was also studied as a function of fiber content under different loading conditions. The fracture behavior of the composite was investigated [11]. Starch-based composites reinforced with jute strands were obtained by injection molding procedure. Jute strands were treated by alkalinisation to increase the strength and the stiffness of composites [12].

The aim of this work is to determine the influence of alkaline treatment and silane coupling agent on hemp hurds and make a comparison on mechanical properties of hemp–starch composite before and after surface treatments.

2. Materials and methods

Technical hemp hurds KANABAT were grown by la Chanvrière de l'Aube (France). They were kept in a conditioned room at 23 °C and 50% relative humidity. In order to enhance the adhesion between hemp hurds and the polymer matrix, hemp hurds were subjected to surface treatment with NaOH (alkaline treatment) in the first step and then a silane coupling agent to enhance the compatibility with the matrix. Sodium hydroxide NaOH, (3-glycidyloxypropyl) trimethoxysilane and acetic acid CH_3COOH were purchased from Sigma Aldrich Chemie GmbH.

Native wheat starch NATILOR was provided by Chamtor company (Pomacle, France). It was stored at 50% relative humidity prior to use. The heating of starch granules in water or aqueous plasticizer results in the gelatinization process caused by irreversible swelling of granules and the mixture forms the binder.

2.1. Chemical treatments of hurds

2.1.1. Treatment with NaOH

Hemp hurds were soaked in two different solutions: 1 wt.% NaOH aqueous solution and 6 wt.% NaOH aqueous solution.

For the 1 wt.% NaOH aqueous solution, they were soaked for 72 h and then neutralized by 1 wt.% CH_3COOH acetic acid aqueous solution. Then, they were washed and rinsed of all the residues of sodium hydroxide until the pH of the supernatant liquid is close to 7. For the 6 wt.% NaOH aqueous solution, hemp hurds were soaked for 48 h, neutralized in 1 wt.% CH_3COOH solution washed and also rinsed of all the residues.

After washing and rinsing of all residues, hemp hurds were dried at 60 °C for 48 h in a convection oven.

2.1.2. Treatment with a silane coupling agent

An aqueous solution of (3-glycidyloxypropyl) trimethoxysilane (GPTMS) in deionized water at 1 wt.% was prepared as a coupling agent. The pH of the solution was adjusted to 2.9 using glacial acetic acid and then left for 15 min until the solubilization. Hemp hurds were soaked for an hour in the solution, washed with deionized water and then dried at 60 °C for 24 h in a convection oven.

The Table 1 gives the significance of nomenclature and abbreviations used for different chemical treatments of hemp hurds.

2.2. Preparation of the hemp–starch concrete

Unmodified wheat starch swells in water at 80 °C and gives the matrix binder. This leads to starch solubilization as amylose leaches from granules and amylopectin becomes fully hydrated [13].

The mixture of the binder contain: 40 wt.% of wheat starch and 60 wt.% of water. Hemp hurds were mixed with wheat starch binder at a hemp/starch ratio equal to 3.3 by weight. The following protocol was adopted [14]:

- Insert hemp hurds in the mixer.
- Add the mixture of the binder: 60% of wheat starch and 40% of water.
- Mix for 10 min.

Hemp–starch mixture is then compacted under a pressure of 0.25 MPa into the molds of 100 × 100 × 100 mm^3 for compressive tests and 100 × 100 × 400 mm^3 for flexural tests. The fresh density is about 240 kg/m^3. Samples were dried in a room with controlled conditions at 23 °C and 50% relative humidity.

2.3. Characterization

In order to characterize different modifications of the surface of hemp hurds before and after treatments, different measurements were done using scanning electron microscopy (SEM), differential thermal analysis (DTA), thermogravimetric analysis (TGA) and infrared spectroscopy (FTIR).

A scanning electron microscopy (SEM) was used to examine the effects of chemical modifications upon the shiv surface. Samples are obtained by cutting small pieces of hemp hurds and sticking them on a carbon adhesive. They were mounted on SEM stands and coated with argon ion sputter with a LEICA EM SCD 050 instrument and then observed at 15 kV by SEM to examine the morphology of hemp hurds.

Differential thermal analysis measurements were performed under dry atmosphere using a DSC 204 F1 instrument (NETZSCH). Temperature ranged 20–450 °C with a heating rate of 5 min^{-1}.

The pyrolysis was carried out with a TGA 207 F3 (NETZSCH) instrument. The sample was heated up to 800 °C at a constant heating rate of 5 °C min^{-1} in an inert atmosphere.

Attenuated total reflectance spectroscopy (ATR) was performed by using a Perkin-Elmer spectrometer. A total of 10 scans were taken for each sample between 500 and 4000 cm^{-1}, with a resolution of 4 cm^{-1}.

Table 1
Nomenclature used for different treatments of hemp hurds and abbreviations.

Keyword	Description
L	Starch binder
NT	Untreated hurds
S1	Treated hurds with 1 wt.% NaOH aqueous solution
S6	Treated hurds with 6 wt.% NaOH aqueous solution
GPTMS	Treated hurds with 1 wt.% aqueous solution (3-glycidyloxypropyl) trimethoxylsilane
NT-GPTMS	Treated hurds with1 wt.% of silane coupling agent
S1-GPTMS	Treated hurds with1 wt.% NaOH aqueous solution and then a silane coupling agent
S6-GPTMS	Treated hurds with 6 wt.% NaOH aqueous solution and then a silane coupling agent
NT-L	Untreated hemp–starch composite
S1-GPTMS-L	Treated hemp–starch composite, with 1 wt.% NaOH and then silane coupling agent.