All natural high-density fiber- and particleboards from hemp fibers or rice husk particles

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Abstract

In the present study, long hemp fibers and rice husk particles have been used for producing all natural-based boards for building, automotive and in-door furniture, employing a simple and economic transformation process (namely, compression molding). In order to have the required consistence and mechanical strength, cornstarch was employed as binder. By this way, fiber- and particleboards have been prepared and characterized in terms of morphology, mechanical properties (flexural modulus and strength). The influence of different relative humidity levels on composite storage modulus and heat deflection temperatures has been investigated, as well. Long fibers turned out to be capable of sustaining approximately three times the load with respect to particles in standard conditions.

Thermal, hygro- and photo stability of the above materials have been investigated under three ageing conditions: namely, i) high temperature (*thermal ageing*), ii) humidity plus high temperature (*hygro-thermal ageing*) and iii) UV radiations (*photo ageing*). Regardless of the experimental ageing conditions adopted, fiberboards have shown good mechanical stability with a modest decrease of storage modulus (< 20%) with respect to the values before exposure.

Keywords: hemp fiber; rice husk; starch; thermo-mechanical properties; ageing.

1. Introduction

Lignocellulosic (LCs) materials from renewable sources are "bio-materials" that have been used in the preparation of composites since historical times [1-4]. However, due to the superior properties of synthetic fibers and unavailability of comprehensive data on durability of different materials, the use of LCs in composites decreased until the 1980s. Recently, a renewed interest has been given to natural materials for counteracting environmental problems and resource consumption [5, 6]. Indeed, lignocellulosic fibers and crops have been considered as an appealing alternative to the conventional reinforcing agents, namely, for some applications in: i) *building* as partial replacement of concrete [7], ii) *automotive* to reduce car weight [5], iii) *furniture* to replace wood [8-17], iv) *packaging* [6, 7, 18-22] and v) *textiles* (e.g. geotextiles and nonwoven textiles) [23, 24].

For bio-construction applications, lignocellulosic by-products such us rice husk [13], wooden particles, annual bast plant waste such as shives [25, 26] banana bunch [27] maize husk, paddy straw, maize cob, coconut coir/pith and groundnut shell [28] have been successfully used for the design and manufacture of fiberboards and particleboards. Unfortunately, all these by-products are not self-sustaining, and hence a binder is mandatory. Soybean protein [29] and starch [8, 9] are examples of renewable source "bio"-binders employed for making particleboards. However, only few materials have been industrially developed, with most of their development still limited to laboratory scale. This fact is mainly to be ascribed to their susceptibility to moisture, temperature and light. Indeed, environmental exposure may cause the degradation of these materials with a detrimental failure of mechanical properties, dimensional instability, and fading [30]. As an example, photo-degradation from environmental UV radiations has shown to worsen the damage induced by hygro-thermal effects alone [31-33]. In general, the effect of weathering on fully bio-based composites has

55 received very little attention in the literature and few publications are available on this topic
56 [31-34].
57 In the present work the production of natural-based boards from the recycle of hemp fibers
58 and rice husk particles is presented. Once panels have been produced the morphology,
59 mechanical properties and moisture absorption kinetics have been assessed and compared
60 with the standard features of materials for interior furnishings.
61 A thorough durability study of the boards subjected to high temperatures, moisture and light
62 exposure for extended periods of time, has been carried out to predict property changes during
63 service.
64

65 **2. Materials and methods**

66 2.1 Materials
67 Hemp long fibers (H) and rice husk particles 0.1-1 mm (R) kindly supplied by Assocanapa
68 s.r.l. and S.P. S.p.A., respectively, were used as received. Cornstarch (CERESTAR® RG
69 03408, 25-28% of amylose content) (S) was purchased from Cargill Inc. Before board
70 preparation, hemp fibers, rice husks and starch were dried at 80°C in a convection gravity
71 oven for 3 h.
72

73 2.2 Board preparation
74 To minimize the final product costs, avoid environmental impact and to perform the easiest
75 preparation process, the raw materials were used without any chemical pre-treatments.
76 The fiber and particle boards were prepared by impregnation of hemp fibers and rice husk
77 with a starch water solution, followed by compression molding in a 50 x 50 x 1 mm^3 mold
78 (**Figure 1**). The starch solution viscosity suitable for optimized impregnation of both hemp
79 fibers and rice husk was obtained with a solution made by 1.5 water to starch weight ratio.

To optimize the coherence of the board and limit its porosity, the mold was loaded with 2.0 g of rice husk impregnated by suspension in 5 g of starch solution (**Figure 2a**) whereas hemp fibers were beforehand pressed at 150°C and 10 MPa in the mold for 2 min to produce a mat (**Figure 2b**). Then, the parts protruding from the mat were cut (**Figure 2c**) and 2.5 g of the compacted mat were impregnated in the mold with 5 g of the starch solution (**Figure 2d**). The composition of the crude boards is reported in **Table 1**.

The fiber and particle boards were prepared by applying 10 MPa pressure to the mold while the temperature was raised from 110 to 140°C for 6 min. and the mold was continuously opened and closed in order to allow water evaporation. At the end of this procedure, a pressure of 10 MPa was kept for 1 min. Finally, the mold was cooled down to room temperature and the sample removed from the mold (**Figures 2e** and **2f**).

An apparent density of 960 and 975 kg/m^3 for H-S and R-S boards, respectively, was calculated as weight/volume ratio (**Table 1)** which allows them to be classified as high-density boards (>800 kg/m^3), according to the ANSI A208.1 standard [35].

Since the processing procedure cannot avoid partial leaking of the material from the mold during hot pressing, final starch and hemp or rice husk content of the boards had to be measured to calculate void content of the boards. To this purpose, starch was solubilized by water extraction from the board by water immersion (500 ml) at 50°C for 24 h and hemp or rice husk were then separated by centrifugation. This procedure was repeated to complete fillers recovering, requiring 3 treatment cycles followed by drying at 80°C for 3 h. Approximately 12 and 10 wt.-% of S was lost during processing with H and R, respectively as shown by the final "effective" percentages calculated and reported in **Table 1**.

On the basis of respectively measured 1240, 1260 kg/m^3 density values for hemp fibers, rice husk and reported 1500 kg/m^3 from the supplier for starch, the board void contents of **Table 1** is calculated.

On the basis of the calculated densities for hemp fibers and rice husk (1240 and 1260 kg/m^3, respectively) and that reported for starch by the Supplier (1500 kg/m^3), the board void contents was assessed and reported in **Table 1**. Io la cambierei così.

2.3 Board characterization

The morphology of boards gold-metallized cross sections was examined using a LEO-1450VP Scanning Electron Microscope - SEM - (beam voltage: 20 kV) and an elemental analysis was carried out by EDX (Energy Dispersive X-ray spectroscopy) using a X-ray probe (INCA Energy Oxford, Cu-Kα X-ray source, k=1.540562 Å)

Three point bending tests were performed at room temperature (23±1°C) and 50% R.H. by using a Zwick Roell Z100 machine equipped with a 5 kN load cell according to EN 312 standard. The tests were carried out using 5 mm diameter supports and actuator with a span of 45 mm and a deformation of 2 mm/min. Three specimens were used for each formulation and the average values with corresponding standard deviations were calculated. These tests provided the flexural modulus (E) and maximum strength (σ) values of the materials. Prior to flexural tests, all samples were conditioned at 23±1°C) and 50% R.H., in a climate-controlled chamber to constant weight (≥ 3 days).

Dynamic Mechanical Analysis (DMA) was performed using a DMA Q800 (TA Instruments) in bending configuration.

2.4 Moisture absorption at room temperature

Moisture absorption by mold samples (50 x 50 x 1 mm^3) dried in a gravity convection oven at 80°C for 48 h, exposed at 23±1°C and 25, 50 and 75% R.H., obtained using supersaturated distilled water solutions of magnesium chloride, sodium dichromate and sodium chloride, respectively, was calculated by time programmed weight control to constant weight. The

130 measurements were duplicated and average values were expressed as weight percentage
131 increase with respect to the initial weight under dry conditions.
132 Storage modulus (E') as a function of temperature was measured using a bending
133 configuration from 30 to 120 ºC, heating rate 3 ºC/min, 1 Hz frequency and 0.05% oscillation
134 amplitude in strain-controlled mode. Measurements were repeated twice and standard
135 deviation was calculated. The Heat Deflection Temperature (HDT) was measured as the
136 minimum temperature at which a material modulus decreases to 800 MPa [36].
137
138 2.5 Accelerated thermal and hygro-thermal ageing
139 Board samples (T3) accelerated thermal aging was carried out in a convection gravity oven at
140 80°C. However, since the elevated temperature of the test tends to reduce the moisture content
141 of samples to levels far lower than those of boards application conditions, extrapolation of
142 aging behavior from the accelerated test to use conditions, might lead to erroneous
143 conclusions. In order to evaluate the additional effect of water on the board ageing at high
144 temperature, board specimens (T1) were also aged at 100% R.H. and 80°C by exposing to
145 saturated vapor in a closed vessel.
146 The samples aged at 100% R.H. were dried at 80°C for 20 min, corresponding to residual 1.6
147 % water content, because they were too soft for direct DMA measurement owing to water
148 plasticisation.
149 The acceleration factor for thermal aging tests was calculated using literature proposed
150 equation (1) [37] [38] [39]:
151 $$f = 2^{\Delta T/10} \text{ with } \Delta T = T - T_{\text{ref}}, \qquad \text{Equation (1)}$$
152 where T_{ref} is the temperature at which the effects of aging are determined and T is the high
153 temperature used to accelerate these effects.

154 Considering the set temperature T at 80°C and the T_{ref} at 25°C, the calculated f factor for
155 thermal ageing is 45.
156
157 2.6 Accelerated photo ageing
158 The photo stability of the prepared boards was investigated exposing two specimens (UV1
159 and UV2) for each formulation, to UV radiations ($\lambda > 290$ nm) at 60±2°C in air using a
160 SEPAP 12/24 unit by ATLAS, characterized by an acceleration factor (f) typically ranging
161 between 4-10 [40] [44], depending on material chemistry.
162
163 2.7 Aging assessment
164 Visual observation was focused on the presence of cracks on the aged specimen surface or
165 detachment/delamination of the fillers and mechanical properties changes were monitored by
166 DMA.
167 Non-destructive isothermal tests at room temperature (25±1°C) every 4-5 days of exposure
168 were performed at 1 Hz and 0.01% of oscillation amplitude in strain-controlled mode. For
169 each formulation, two specimens were tested in each condition in order to check the
170 reproducibility.
171 The same conditions of thermal ageing were carried out with a 20 h sampling frequency.
172
173 **3. Results and Discussion**
174 3.1. Morphological characterization
175 In the SEM micrographs of **Figures 3a** and **3b**, a wide size distribution for both fibers and
176 particles is observed. Hemp fiber section varies from 1 to 200 μm, while rice husk particle
177 size ranges from sub micrometric to 1 mm ~~size~~. The elemental analysis of inorganic elements
178 by EDX has detected traces of Mg, P, K and Ca ions in the hemp fibers and an abundant

179 presence of Si in the rice husk, more concentrated on the husk external part, as stated in the
180 literature [19].
181 As far as fiberboards are concerned, a homogeneous interconnection of hemp fibers due to the
182 presence of starch is noticed (**Figure 3c**). The continuous pathway does not allow
183 distinguishing single fibers. Conversely, in the case of rice husk it is simpler to identify the
184 particles in the cross section. Indeed, the spongy surface is mainly made by rice husk particles
185 (point 4 in **Figure 3d**), alongside the starch area (point 5 in **Figure 3d**).
186
187 3.2 Three point bending tests
188 A flexural modulus of 1300±300 and 5200±1000 MPa as well as a maximum strength of 16±2
189 and 64±18 MPa were found for R-S and H-S boards, respectively. Exemplificative curves of
190 the test are reported in **Figure 4** with a digital picture of the specimens at the end of tests. It is
191 clear that the two boards displayed a different failure behavior. In particular, R-S exhibits a
192 brittle fracture (stress at break of 16 MPa) without plastic deformation. At the end of the test,
193 the specimen appears to be broken in different parts (*see* related picture in **Figure 4**). On the
194 contrary, H-S reaches a significantly higher stress at break (i.e. > 50 MPa) and, after the
195 failure hemp fiber network still sustains the broken board parts (*see* related picture in **Figure**
196 **4**) resulting in a slow decrease of stress.
197 According to the EN 312 standard for particleboards (in particular, type P2 for interior
198 fitments, including furniture in dry conditions), both boards satisfy the requirements of 13
199 MPa for what concerns the strength, but only fiberboards exhibit the recommended modulus
200 of 1800 MPa [41].
201
202 3.3 Moisture absorption
203

The moisture absorption affects the boards properties and it represents one of drawbacks to be overcome; hence it is important to investigate the kinetics of their moisture absorption and the corresponding mechanical properties [19] [42] [43] [44].

Hemp fibers and rice husk particles exhibit a rapid moisture absorption, reaching the equilibrium with the same weight gain: 6.7± 0.5 % after 1 day exposure at 23°C and 50% R.H (**Figure 5**). Although the rate of water absorption by the boards is reduced compared to pure fillers, as shown in **Figure 5** for R.H. 50%, the equilibrium value of the H-S and R-S boards which is comparable, is also reached in 1 day showing a 2.4 times increase on going from 25 to 75 % R.H. (**Table 2**). It must be noticed that the moisture content for all samples is, however, still under the limit of the EN 312 standard for boards [41] which sets a weight gain maximum threshold at 13% for a relative humidity of 65% and a temperature of 20°C, that are less severe conditions with respect to those adopted here (namely, 23°C and 75% R.H).

The storage modulus (E') for H-S and R-S boards either original dry or aged at 25, 50 and 75% R.H. and 23°C is plotted in **Figures 6a** and **6b** as a function of temperature. It is seen that hemp fibers have a reinforcing effect which is about 2 times that of rice husk on a weight basis, which can be primarily explained by the different aspect ratio of fibers and particles.

Although H-S and R-S absorb a comparable amount of water on aging (**Table 2**), absorbed water has an opposite effect on the two types of materials. Indeed, upon aging, R-S boards show an expected progressive decrease of modulus up to 30%, after exposure to R.H. increasing from 25 to 75%. A surprising progressive increase of modulus is instead found upon exposure of H-S boards to increasing R.H. environment, reaching an astonishing 1.35 times increase at 75% R.H. The reason for the unexpected behavior of H-S boards is likely to depend on effect of absorbed water on the hemp-starch interface or hemp fibers, the mechanism of which is worth to be further investigated.

On increasing temperature, R-S boards, either original or aged at 25 and 50 % R.H., show a regular linear decrease of the modulus to values ranging from 1300 to 1100 MPa. In the case of the R-S board aged at 75% R.H., the linear decrease is followed by a sharp fall of modulus to 600 MPa.

A more complex trend is shown by the H-S boards which show a crossover of the curves modulus-temperature at about 70-80°C. However, also for H-S boards, a linear decrease of modulus is observed to 2600-2100 MPa upon aging at 25 and 50 % R.H and a more severe fall to 1500 MPa for specimens aged at 75% R.H.

The trends of R-S and H-S samples aged at 25 and 50 R.H. are due to the presence of absorbed water since the trend of the original material is recovered upon sample drying. Whereas, in the case of samples aged at 75% R.H., the trend is a consequence of material ageing due to the action of absorbed water because the original trend is not recovered upon sample drying.

The E' values exhibited by the two boards are considered suitable for applications where high rigidity is required at room temperature. Furthermore, thanks to the study carried out at different R.H., it is possible to select the crop to be incorporated in the board on the basis of the moisture expected in the application. Indeed, at high relative humidity levels, hemp fibers are the best choice; conversely, at low humidity content rice husk particles could be an acceptable choice if the required mechanical performances are satisfied.

Figures 6a and **6b** show that H-S and R-S boards either original or after aging up to 75% R.H. are characterized by an HDT value above 120°C apart from R-S board aged at 75% H.R. which HDT is 97°C. Thus, the boards are suitable for applications at relatively high temperature as for example in automotive under hood or sun exposed components.

3.5 Thermal, hygro-thermal and photo ageing

253 The thermal and hygro-thermal ageing of the prepared boards has been followed for 50 days
254 that correspond to circa 2250 days (6 years) of long-term ageing at room temperature,
255 following the Equation (1) and using a f factor of 45. The photo-thermal ageing has been
256 followed for 40 days (960 h of exposure) that correspond to about 3-7 years of solar exposure
257 in continental climate (f factor of 4-10) [40] [45]. The effect of these different ageing
258 conditions on the proposed materials has been monitored by DMA (**Figure 7**). In order to
259 compare specimens having different modulus (E'_0), all curves have been normalized in dry
260 conditions and the resulting E'/E'_0 ratio plotted as a function of time. **Figures 7a** and **7b**
261 report these trends for samples subjected to thermal and hygro-thermal (T3 and T1) and
262 photo-thermal ageing (UV1 and UV2), respectively.
263 As far as samples exposed to thermal ageing are concerned, a general reduction of composite
264 stiffness has been observed both in dry conditions and humid environment (**Figure 7a**). More
265 specifically, the H-S-T1 sample aged with 100% of R.H. behaved similarly to the dried
266 homologous H-S-T3 with a reduction of E'/E'_0 lower than 15%. R-S sample exhibited a
267 similar behavior to that of H-S in dry conditions (*compare* R-S-T3 with H-S-T3 curves).
268 Conversely, it showed a faster property failure when aged at 100% of R.H. (R-S-T1 sample).
269 Indeed, after 37 days, 80% of E'/E'_0 reduction with respect to the initial conditions has been
270 observed and it was not possible to further carried out this measurement because of R-S
271 fracture.
272 As far as photo-thermal ageing is considered, UV1 and UV2 samples exhibited a restrained
273 reduction of composite stiffness during exposure (**Figure 7b**). Indeed, at the end of test, after
274 40 days of exposition, the reduction is less than 20% for both samples with respect to the
275 starting value.

The effect of ageing on optical characteristic of the samples is mostly evident in the case of hygro-thermal ageing which leads to browning (R-S and H-S), warping (H-S) or delamination (R-S) as shown in **Figure 8**.

The collected results from the ageing tests demonstrate that an effective application in building, automotive and outdoor furniture could be foreseen, as the board degradation due to temperature, hydrolysis and UV radiation turns out to be very slow at room temperature, and board life expectancy exceeds 3 years in the worst forecast conditions.

4. Conclusions

In the present study two different lignocellulosic by-products (hemp long fibers and rice husk particles) have been used to produce all natural-based boards (fiber- and particleboards) by using cornstarch as binder. A simple and economic transformation process based on the use of hot compression molding has been exploited.

Fiberboards have proven to be stiffer than particleboards (twice as much) and able to sustain more than three times the load, confirming the morphological observations that indicated a higher interconnection between hemp fibers and starch with respect to that evidenced between rice husk particles and starch. At 50% R.H. both boards satisfy the requirements of 13 MPa for what concerns the flexural strength, while only fiberboards exhibit the recommended modulus of 1800 MPa for interior fitment.

Thanks to the highest mechanical properties, the H-S composite can be considered fully eligible for applications in building and furniture. Furthermore, the HDT evaluation extends its application even at high temperature applications, such as in automotive.

Different relative humidity levels significantly affected the composite modulus: R-S boards show an expected progressive decrease of modulus up to 30%, while a surprising progressive

300 increase is found for H-S boards, reaching an astonishing 35% of increase after exposure to
301 R.H. increasing from 25 to 75%.
302 Finally, the prepared boards have been subjected to different accelerated aging conditions and
303 durability has been measured in terms of modulus reduction.
304 Results have also evidenced a general decrease of composite stiffness for the ageing
305 conditions employed in this work (namely, thermal, hygro-thermal and photo ageing).
306 However, for both fiber- and particleboards the stiffness reductions due to thermal ageing
307 after 50 days (corresponding to 6 years at room temperature), and due to photo ageing after 40
308 days (3-7 years equivalent) have been only lowered by 15 and 20%, respectively.
309

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