Exploring *Ulex europaeus* to Produce Nontoxic Binderless Fibreboard

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Ulex europaeus is one of the most abundant and aggressively invasive plants on the world. Its fibres, which can be isolated using an alkaline pulping process, have been successfully thermo-pressed into high-density fibreboards without any type of binder. The influence of the bioorganic and crystalline components on the product was investigated using crystallographic, thermo-analytical, and mechanical techniques. Cellulose was predominantly an I_β polymorph, more common in hardwood, but the composition of the material was typical of softwood. Both the crystallinity in the fibres and the average domain size of cellulose increased during thermo-pressing. Notwithstanding that the residual lignin was present in a small amount, this promoted the cohesion of fibres by improving hydrolysis and adhesion properties. The best overall properties were observed in the pressed products of 1030 ± 38 kg/m^3, showing an elastic modulus of 4.31 ± 0.26 GPa, with a modulus of rupture of 26.5 ± 1.3 MPa. These results serve as the basis to transform the invasive species into a fully non-toxic added-value resource.

Keywords: Bioresources; Biofibers; Cellulose; Fibreboard; Green materials; Gorse

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INTRODUCTION

Ulex europaeus (Gorse or Furze, *Ulex* in the following) is a prickly, flowering, perennial evergreen shrub native to central Europe. It is a hardy plant with a fast edapho-climatic adaptation, a high reproductive capacity, and a lack of natural enemies, making it one of the most aggressive invasive species of native landscapes and agriculture. The plant has a major global economic impact; there are actions aimed at limiting its expansion or eradicating it (Gaynor and MacCarter 1981; Radclife 1986; Matthei 1995; Foxcroft *et al.* 2017). A possible economical alternative is to exploit *Ulex* for the production of fodder, biomass, or biofibres.

Biofibres, in particular cellulose fibres, can be the basis for value-added products such as fibreboards. The fibreboards can be particularly important in countries with large climatic variations or serve as alternatives to more traditional products. The bonding of cellulose fibres is a major issue. The use of formaldehyde-based resins, or other chemicals, for the production of boards using a dry process can have consequences on human health (Duong *et al.* 2011). A sustainable dry binderless process is not yet available for low- and mid-density fibreboards.

The situation changes in hardboards (high-density fibreboards), where a wet process promotes the self-adhesion of cellulose fibres. In particular, a thermomechanical

pre-treatment under moist conditions can hydrolyse the hemicellulose and plasticise the lignin. Spalt (1977) obtained encouraging results with this process that greatly improved the properties of the pressed products. These properties relate to the composition of the starting material (hemicellulose and lignin contents in the fibre) and the process temperature. However, the hemicellulose is critical, as it might caramelize at the process temperature (Maillard reaction), thus degrading the properties of the consolidated material (Velásquez *et al.* 2003; Peterson *et al.* 2010; Zhang *et al.* 2015).

The possibility of using the cellulose of *Ulex*, and in general of exploiting the invasive species for the production of fibreboard or added-value products, has not yet been explored. In this study, the bio-organic components in the stem of *Ulex europaeus* were examined (Ligero *et al.* 2011; Ares-Peón *et al.* 2013; Celis *et al.* 2014) and a suitable thermo-mechanical treatment was developed, leading to the self-adhesion of cellulose fibres. A green and sustainable route was created for the production of fibreboard, involving only the chemicals that are already exploited in pulping processes by the papermaking industry. The resulting products were classified by their density as high-density fibreboard (HDF) according to ISO 16895-1 (2008) or as high-density medium board (MB)/hardboard (HB) according to DIN EN 316 (2009). The starting material and the resulting fibreboard were thoroughly tested structurally, thermally, and physio-mechanically to evaluate the process's market readiness and its compliance with relevant standards.

EXPERIMENTAL

Starting Fibres and Components

Ulex europaeus (Fig. A1) specimens of approximately 6 to 7 years of age were taken from the Santa Rosa Experimental Farm located in Cabo Blanco, Valdivia, Chile. The specimens were cut to 30 to 80 mm using a chipper with no discrimination of shape, size, or anatomical parts (Fig. A2). The chips were then reduced to less than 10 mm with a PZ-8 Chipper Machine (PallMann, Clifton, NJ, USA).

The quantitative determination of the hemicellulose, cellulose, and lignin content was performed in *Ulex* stems according to Polyak's method (1948), the Kurschner-Hoffer cellulose method (1931), and TAPPI T 222 om-88 (1988), respectively. An extraction in both cold and boiling water with 1% NaOH, ethanol, and toluene was also performed according to TAPPI T 204 om-88 (1988). The quantification of the bioorganic components in the fibres was completed following the ASTM standards for cellulose (ASTM D1103-60 1977), lignin (ASTM D1106-96 2013), ashes (ASTM D1102-84 2013), extractive (ASTM D1105-96 2013), and moisture (ASTM D4442-07 2007).

Extraction of the Fibres

A thermo-alkaline pulping process was employed to extract the cellulose fibres from the reduced biomass (Fig. A3). This thermo-chemical treatment, similar to that already successfully employed by some of the present authors (Celis *et al.* 2014), consisted of mixing the chips wood in a Mini-mill digester (MK System Inc., Peabody, MA, USA) with an aqueous solution (40 g/L) of NaOH. The quantity was chosen assuming a 10% rate of fibre release, *i.e.*, a Kappa number lower than 67. Heat was then applied to remove the lignin from the fibres and promote defibreing in the chips (Casey 1990). The process was performed under the constant conditions of NaOH concentration, pressure, temperature,

and time. Following this process, an actual yield of approximately 75% was obtained, *i.e.*, a Kappa number of 22.

Hot Pressing of the Fibres

The dry fibres were employed to create 18 square boards of approximately 430 mm of side and 7 mm of thickness for each set of apparent densities (Table 1).

Table 1. Characteristics of the Fibreboards and Cellulose Crystallinity

Apparent Density (kg/m^3)	Final Density (kg/m^3)	Quantity of Dry Fibres (g)	Pressing Time (min)	CI (%)	Cx (%)	DS (nm)
Fibre	--	--	--	75	42	2.9
800	855 ± 22	1035	20	80	51	4.2
850	921 ± 18	1100	18	81	50	4.3
900	935 ± 18	1165	15	82	52	4.3
950	1030 ± 38	1230	13	81	52	4.2

*Notes: Pressing time (per board), Crystalline index (CI), Crystalline portion (Cx), and the Average domain size of cellulose according to Scherrer formula (DS)

The various amounts of dry fibres for each board (Table 1) was disaggregated in 2 L of water and manually homogenized. The slurry was poured over a square metal mesh with an opening of 2.0 mm inserted in a square wooden mould of 430 mm length and 200 mm depth (Fig. A4). The pre-pressing was performed in a conventional 10-ton hydraulic press to remove the excess water and retain approximately 30% moisture. The resulting fibrous blanket was then cold-pressed in a LA 160 63/63 hydraulic press (Robert Bürkle & Co., Freudenstadt, Germany) for 3 min at a constant pressure of 5 MPa. The temperature was then raised to 200 °C under the same load, and the specimen was left there until there was no more steam (*ca.* 13 min to 20 min, Fig. A5-A6). This last step activates the natural binder of the *Ulex* fibres.

X-ray Diffraction Analysis

A portion of the Ulex fibres was dried at 60 °C for 24 h in an ED53 chamber oven (BINDER GmbH, Tuttlingen, Germany). Aliquots of 1 g of this sample were pressed in a 25-mm diameter die at 4 kPa for 5 min. The disks were mounted on the spinning sample holder (15 rpm) of a D2 Phaser diffractometer (Bruker, Karlsruhe, Germany). The machine employed Ni-filtered Cu radiation (30 kV and 10 mA), a divergence slit of 1 mm, an antiscatter slit of 1 mm, Soller slits of 2.5°, and a LYNXEYE detector. The alignment was regularly checked against the NIST SRM1976 alumina plate standard. Patterns were collected in the 5° to 45° range, counting 5 s/0.01° steps.

The Z-discriminant function of Wada and Okano (2001) was employed to identify the major presence of the I_β cellulose polymorph. The crystalline index (*CI*) was calculated according to the method of Segal *et al.* (1959). The crystalline portion (*Cx*) was calculated from the integrated intensity of the amorphous and crystalline phases contribution to the total diffraction pattern, assuming that the effect of the absorption was irrelevant (Klug and Alexander 1974; Zevin and Kimmel 1995).

The crystalline domain size of the I_β cellulose was calculated *via* the Scherrer (1918) equation from the (002) reflection, to provide commonly quoted results (Garvey *et al.* 2005). The alternative whole powder pattern modelling (WPPM) (Scardi and Leoni 2002), which gives a more physical quantitative result, was also tentatively employed. The

patterns were modelled using PM2K software (University of Trento, Trento, Italy) (Leoni *et al.* 2006). This was the first time that a complex material like cellulose was analysed with these advanced methods.

To ensure comparative and a minimum statistical validity, each analysis was repeated on at least two independent specimens, confirming a significant homogeneity of the samples, reporting similar values for every set of the different apparent densities. The WPPM modelling was unsuccessful. The patterns deviated too much from an ideal structure: the available microstructure models were unable to model the peak position displacement, and the observed peak shape and broadening. The static displacement was probably too severe to be considered by the available microstructure models. Further investigation is needed, due to the quantitative validity of the Scherrer (1918) formula's results, which was in any case, highly questionable for a real material where a distribution of sizes (easily considered within the WPPM approach) was expected. Thus, the Scherrer formula (1918) was valid only for comparison purposes, but not for a true quantitative assessment of the domain size of cellulose.

Thermal Analysis

Differential scanning calorimetry (DSC) was performed on 1.6 mg of *Ulex* fibres in a DSC-Q20 calorimeter (TA Instruments, New Castle, DE, USA) with alumina crucibles. The data were recorded in the ramp at 10 °C/min from 25 °C to 450 °C in a controlled atmosphere of 50 mL/min of N_2 and 50 mL/min of dry air. The calorimetric data were processed using Platinum Software (TA instruments).

Physical and Mechanical Characterization

The density of the pressed products was determined according to BS EN 323 (1993), and results were compared using the analysis of variances (ANOVA). The thickness swelling (TS) and water adsorption (WA) were estimated according to BS EN 317 (1993). These procedures were performed on square test specimens of 50.1 mm ± 0.3 mm length and 6.7 mm ± 0.1 mm of thickness.

A universal testing machine model WDW-10E (TIME Group Inc., Beijing, China) was used to determine the modulus of elasticity (MOE) and modulus of rupture (MOR) according to BS EN 310 (1993). The test samples were sized 193 mm ± 0.2 mm (length) × 50.6 mm ± 0.1 mm (width) × 6.7 mm ± 0.1 mm (thickness). Moreover, the internal bond (IB) test was performed using BS EN 319 (1993) on test samples of approximately 50 mm × 50 mm ± 0.2 mm. Each specimen was conditioned at 20 °C and 65% relative humidity before testing, and the actual dimensions were determined according to BS EN 325 (2012).

RESULTS AND DISCUSSION

Stem Composition

The bioorganic components of *Ulex europaeus* biomass are shown in Table 2; the fibre moisture content is not included. The cellulose, lignin, hemicellulose, extractives, and ash contents were within the range of previous literature values (Jobson and Thomas 1964; Kaloustian *et al.* 2000; Ligero *et al.* 2011; Celis *et al.* 2014). In particular, the cellulose content in Chilean *Eucalyptus globulus* (43.3 wt.%) and *Pinus radiata* (45.6 wt.%) (Mansilla *et al.* 1991) was lower than in *Ulex europaeus*. These parameters have substantial importance given the similar edapho-climatic conditions of the biomass sources.

Table 2. Composition of the Wet Stem (dry-wood percentages) and Fibres of *Ulex europaeus*

Main Compounds	Stem (wt.%)	Fibre (wt.%)
Moisture content	--	7.47 ± 0.33
Extractive	6.60 ± 0.24	3.36 ± 0.08
Ash	1.46 ± 0.09	1.20 ± 0.02
Lignin	24.50 ± 0.02	18.80 ± 0.71
Hemicellulose	21.70 ± 0.04	29.91 ± 0.21
Cellulose	47.00 ± 0.14	46.74 ± 0.13

The hemicellulose content was comparatively less than in the typical industrial biomass sources (Mansilla *et al.* 1991), whereas lignin was within the characteristic parameters of hardwood deciduous trees (Han 1998). Notably, the high content of extractives (6.6%) was larger than in normal industrial biomass resources. This could be attributed to the high content of tannins, flavonoids, and isoprenoids (Cao *et al.* 1997; Máximo *et al.* 2002) in *Ulex*. This was part of a larger process aimed at using supercritical fluids for the pre-processing of this otherwise unused biomass.

Chemical Composition of the Fibres

As expected, the *Ulex* fibres (Table 2) showed a reduced quantity of substances that are more susceptible to the thermo-alkaline extraction processes. Contrary to the other extractive components, cellulose seemed unaltered by the alkaline process. In contrast, lignin was reduced by about 23%. This was highly unexpected, as the lignin residual usually remains very high in cellulose. This effect was possibly due to the heterogeneous nature of the lignin in *Ulex* (Dimmel and Gellerstedt 2009; Poletto *et al.* 2014). The hemicellulose increased due to the loss of soluble and binder components of the stem in the alkaline environment. It was not possible to deduce the pulping effect on the fibres based on the ash content.

Structure/Microstructure and Thermal Analysis of Cellulose

Figure 1 shows a portion of the XRD patterns of the starting *Ulex* fibres and of the fibreboards consolidated at different densities (Table 1). The features were typical of a mixture of triclinic I_α (space group P1) and monoclinic I_β cellulose (P21) (Gardner and Blackwell 1974; Sugiyama *et al.* 1991; Nishiyama *et al.* 2002). The corresponding ICDD PDF-2 cards for the two cellulose polymorphs were 56-1719 and 56-1718, respectively.

Similar patterns were observed in the native cellulose, even if the position of the (101)/(10-1) doublet (Fig. 1) slightly deviated from the values that were typical for other sources of biomass (Sugiyama *et al.* 1991; Wada *et al.* 1993; Nishiyama *et al.* 2002). This feature could be an interesting element for the phylogenetic identification of this source of cellulose (Atalla and Vanderhart 1984; Sugiyama *et al.* 1991; Wada *et al.* 1993). Furthermore, the broad background in the 2θ range of 10° to 30° came from the amorphous components that were present in the fibres (mainly cellulose).

The Z-discriminant proposed by Wada and Okono (2001) allowed the determination of the predominant cellulose polymorph by analysing the position of the (101)/(10-1) doublet. The result suggested that the cellulose in *Ulex europaeus* was of the cotton-ramie type, characterised by a prevalence of the I_β polymorph. This feature is usually observed in hardwood species.

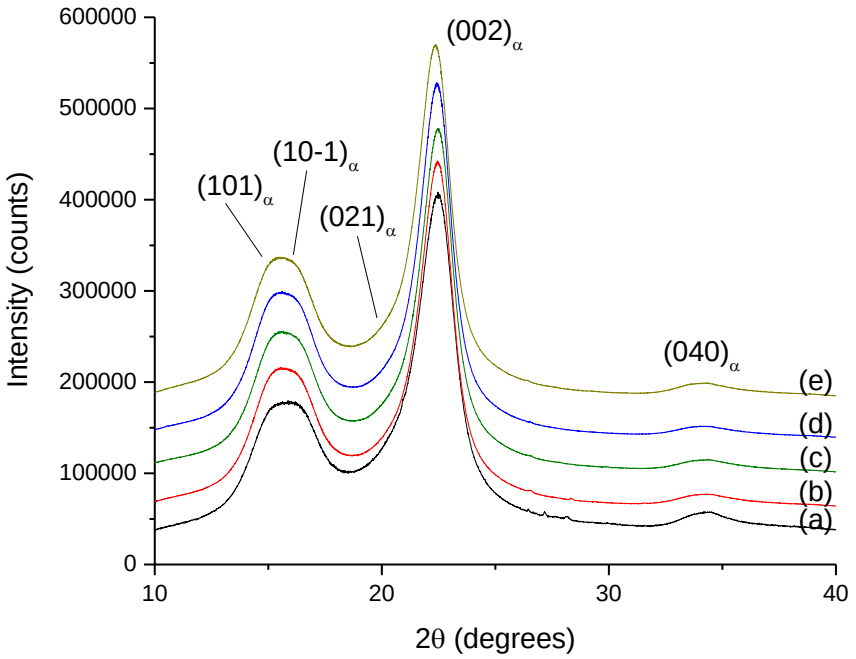

Fig. 1. Diffraction patterns of *Ulex* fibres (a) and of the fibreboards pressed at (b) 800 °C, (c) 850 °C, (d) 900 °C, and (e) 950 °C

The crystalline index of the starting fibres was 75%, whereas in the fibreboard the value ranged from 80% to 82%; therefore, little or no effect of the densification or the pressing process was visible. The domain size of the cellulose in the starting fibres was about 2.9 nm (Table 1). The fibres were therefore made of small I_β domains embedded in an amorphous matrix (Atalla and Vanderhart 1984). This microstructure had a direct influence on the intrinsic properties (Gardner and Blackwell 1974; Atalla and Vanderhart 1984; Sugiyama *et al.* 1991; Wada *et al.* 1993; Cao *et al.* 1997; Máximo *et al.* 2002; Nishiyama *et al.* 2002; Dimmel and Gellerstedt 2009; Leppänen *et al.* 2009; Poletto *et al.* 2014). The change in crystallinity was probably due to the growth of those domains accelerated by the heat involved in the fibreboard consolidation (Salmén 2004).

The DSC data (Fig. 2) showed the evolution of the molecular structure of all of the biopolymers present in the *Ulex* fibres. In the first stage, between 147 °C and 320 °C, a shallow and broad endothermic peak was observed at 229 °C and was attributed to the decomposition of hemicellulose (Tsujiyama and Miyamori 2000; Yildiz and Gümüşkaya 2007). A large endothermic signal followed at 361.74 °C. Magnifying the tip of this peak shows evidence of splitting, with a second maximum at 359.63 °C. This splitting could have been a signature for the process of ordering of the cellulose (Ramiah 1970; Shen *et al.* 2010). A further exothermic peak was present at 405.14 °C, which could be associated with the degradation of cellulose and organic components such as lignin (Raemy and Schweizer 1983). Above *ca.* 430 °C there was a gradual increase of the thermal signal, possibly due to the degradation or phase change of lignin (Shen *et al.* 2010). The lignin was difficult to decompose and its presence could not be directly inferred from thermal analysis alone.

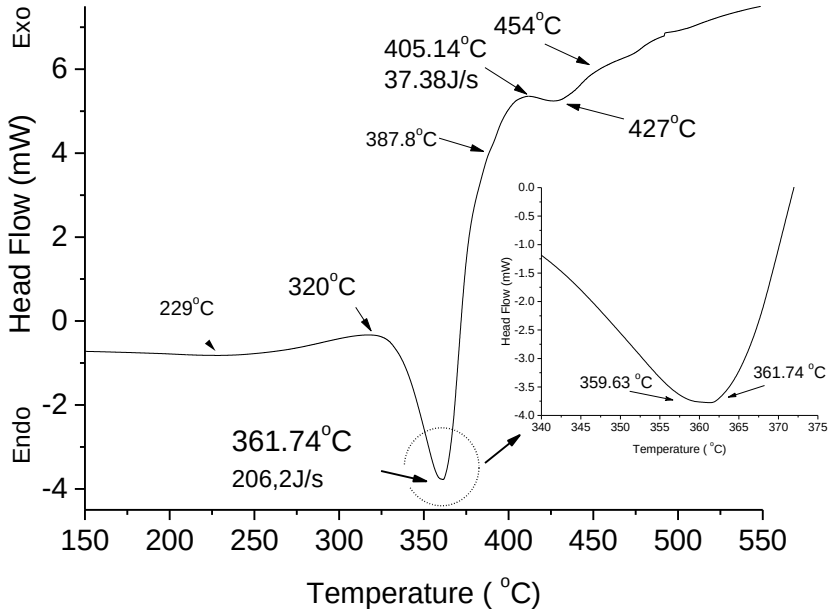

Fig. 2. Thermal analysis on *Ulex* fibres

Physical-mechanical Properties of the Fibreboard

The results of the physical-mechanical characterization of the fibreboards are shown in Table 3. The experimental data response was analysed assuming a normal distribution with a confidence level of 95%. The binderless pressing was performed at four final densities, the real average values of which ranged between 856 kg/m^3 to 1030 kg/m^3 (Table 1). According to these density values, ISO 16895-1 (2008) classifies these boards as high-density fibreboard (HDF). In contrast, DIN EN 316 (2009) classifies them as high-density medium board (MBH) or hardboard (HB), depending on their actual density (400 kg/m^3 to 900 kg/m^3 for MBH and >900 kg/m^3 for HB, respectively).

Table 3. Properties of the Fibreboards after 2 h and 24 h

Density (kg/m^3)	MOR (MPa)	MOE (MPa)	IB (MPa)	WA 2 h (%)	WA 24 h (%)	TS 2 h (%)	TS 24 h (%)
800	13.6 ± 1.1	1963 ± 237	0.45 ± 0.04	107 ± 6	114 ± 6	57 ± 3	65 ± 5
850	18.7 ± 1.5	2866 ± 253	0.56 ± 0.05	95 ± 4	103 ± 4	55 ± 3	63 ± 3
900	19.4 ± 1.4	3014 ± 217	0.65 ± 0.05	85 ± 4	92 ± 1	51 ± 2	59 ± 2
950	26.5 ± 1.3	4306 ± 256	0.88 ± 0.04	80 ± 7	87 ± 7	50 ± 5	58 ± 5

Notes: Modulus of rupture (MOR), modulus of elasticity (MOE), internal bonding (IB), water absorption (WA), and thickness swelling (TS)

The MOR, MOE, and IB increased when the density increased (Table 3). The hot-pressing time had a negligible effect. The temperature played a role: self-adhesion and thus mechanical properties increased when temperature increased. The optimal value seemed to be the one chosen for the proposed process, high enough to activate the adhesion, but still low enough to avoid the caramelisation of hemicellulose that was deleterious in this case. The small size of the *Ulex* fibres conferred a large specific surface area, which improved

the hydrolysis of hemicellulose and ensured the lignin (residual) adhesive effect under the conditions of the process (Spalt 1977; Velásquez *et al.* 2003; Brebu and Vasile 2010). This was the explanation for the mechanical properties. From the thermal analysis, in the lower temperature range hemicellulose could be activated without relevantly affecting other bioorganic components. Cellulose also reacted, which possibly reduced the amorphous phase, especially in the higher density boards, although important changes in the crystalline structure were not observed according to the analysis by X-ray diffraction (Fig. 1).

The MOE of the highest density boards meets the requirements of ISO 16895-2 (2008) for employing the material under dry conditions. The MOR was lower than the standard requirements for its applications in wet conditions.

The WA and TS characterize the dimensional stability of the fibreboard under severe moisture. Both the WA and TS were reduced with increased density of the board (Table 3) due to the porosity reduction caused by the accommodation of the fibres during the hot pressing, leading to a major fibre-fibre adhesion and therefore a minor water permeation. The two parameters did however not reach the minimum value required by ISO 16895-2 (2008) for use in dry conditions.

The increased density of the boards resulted in a reduction of the values of the TS and WA, which were related to the dimensionality of the specimens. These parameters were directly influenced by the presence of hemicellulose which was hydrophilic, low lignin (hydrophobic), and the high space aspect of the fibres, which created an effective interaction between the fibres but generated a greater moisture adsorption (Velásquez *et al.* 2003; ISO 16895-2 2008; Quintana *et al.* 2009).

CONCLUSIONS

1. The invasive plant species *Ulex europaeus* was transformed into an interesting source of biofibres for industrial applications.
2. Fibre extraction using an alkaline pulping process did not alter the cellulose content. Bioorganic components, such as lignin and extractives, were greatly reduced. However, lignin was still present in a reasonable residual concentration in the fibres.
3. The pressing of the fibres and the heat treatment of the pressed mat at 200 ºC under moist conditions led to a dense fibreboard. The treatment promoted self-adhesion of the fibres and increased the size of the crystalline cellulose domains and the crystallinity of cellulose.
4. The large content of lignin and amorphous biopolymers in general is key to the binderless product produced.

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APPENDIX

Fig. A1. Gorse (*Ulex europeaus*)

Fig. A2. Chips Wood

Fig. A3. *Ulex* fibers (fiber characterization [Celis *et al.* 2014])

Fig. A4. Pre-pressing of disaggregated fibers

Fig. A5. Thermal pressing in hydraulic press

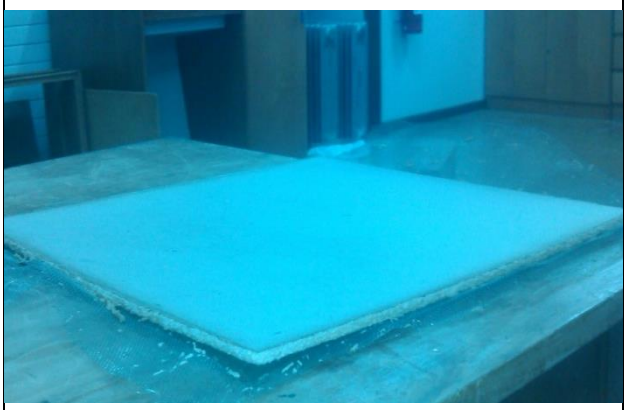

Fig. A6. Fiberboard