

COMPOSITE BOARD PREPARED WITH STRAW

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Abstract

In the past decade the automotive industry has witnessed the remarkable achievements in the field of materials science through the development of sustainable resins and biocomposites. These changes are driven by the needs to reduce the environmental footprint and to reduce the weight of vehicles. Composites made of renewable materials have been vastly used in interior components of passenger and commercial vehicles. Wheat straw, like other natural fibers, such as bast fibers, has also been investigated for composite reinforcement. The purpose of this paper is to develop a cost-effective and feasible manufacturing process of wheat straw - polyester composite pressboard. The straw was prepared in two different sizes: a) short length (<3 cm) and b) particulate; the polyester resin used was Acrodur. The natural heterogeneity of straw and the poor compatibility of its surface with resins are a major challenge to produce quality composites with consistent results. Therefore, this research investigated two relatively low cost methods for surface treatment on the straw. These two surface treatments are named alkaline and boiling water. The effects of treatments were examined by contact angle measurement method to provide insights on the wettability and the absorption of polyester solution on the straw surface. The composites were prepared with ratios of straw to resin in the range of 90% to 60% (straw) using compression molding. Factors investigated included pressure, time and temperature. Finally, flexural properties were measured. Surprisingly, results have shown that particulate straw produced composites with higher flexural modulus than short length straw. This behavior is attributed to the surface composition and impregnation of resin.

Background and Requirements

Due to environment and sustainability issues, in the past decade automotive industry has witnessed the remarkable achievements in the field of materials science through the development of biocomposites. There is a trend in reducing the use of glass fiber by taking advantage of the lower density and cost provided by some natural fibers. Composites made of renewable materials have been vastly used in interior body parts for a number of passenger and commercial vehicles.¹ The natural plant fibers, such as jute, flax, hemp, sisal and ramie, have been used in reinforced plastic composites and greatly lightened the vehicle body by ~60%.¹

As an agro-residue, wheat straw has been gaining more and more attention, due to its abundancy and renewability. However, wheat straw has more complex structure and is less homogeneous in components than other natural fibers, therefore large variations are found in fiber characteristics and properties.² Moreover, straws from barley and oat are very similar to wheat and could potentially be used in combination with wheat straw.

The incompatibility of straw with binder resins along with its inferior strength performance result in the fact that the use of wheat straw has been limited in structural applications. The ineffective wetting caused by outer waxy layer of wheat straw remains a major unsolved technical problem in production of straw board.³ Therefore, the treatments on wheat straw are considered in modifying the surface properties. The wettability of binders on a solid surface can be studied by determining the contact angle and its changing rate. Moreover, the binder spreading and penetrating are also considered as indices for evaluating wetting and adhesion quality.⁴

Many commonly used binder resins, either thermoplastics or thermosets, have been applied

in the production of straw board, to ensure effective stress transfer.⁵ The thermoset binders have stronger binding ability and lower water absorption while offering higher thermal stability at low cost compared to thermoplastic binders.⁶ Phenolic, melamine, epoxies, and urea are some examples of the mostly used thermoset resins. However, stringent regulation of formaldehyde-containing products and limited petrochemical resources have promoted the development of novel alternative binder resins with improved properties and environmental friendliness.⁷

The thermal compression molding technique is utilized in the production of the pressboard. It is low cost, easy setup. When compression molding is applied to thermosetting polymer, the resin is compressed-cured-solidified successively (in a sequential order), where in-situ polymerization is triggered by the increased temperature under pressure. Pressure is exerted to compress the material to form a desired shape and squeeze the resin to fill up the cavity until the resin is solidified after a certain period of applying time. Those production parameters are influential on final properties of end-products.⁸

Surface Treatment and Contact Angle Measurement

The outer thin waxy and silica layer surrounding the straw stem causes ineffective wetting of synthetic resins used as a binder,⁹ and impair the mechanical property of the product. Therefore, the surface treatments are considered to remove undesired components and to ensure effective interfacial adhesion.

Alkaline treatment is one of the mostly used chemical methods for modifying natural fibers. This treatment removes a certain amount of simple hydrocarbons (waxes) and SiO₂ covering the external surface of the fiber cell wall and partially dissolves lignin and/or hemicellulose, thereby increasing chemical affinity to resins and the surface roughness.¹⁰ An alternative method for surface treatment is to simply use hot water, which can be very cost effective and impart significant changes to the surface composition.¹¹

Good wetting is reflected by the even binder distribution on the solid surface. The change of surface hydration property caused by the treatments leads to the contact angle changes when getting contact with a liquid. The measurement of contact angle and its rate of change with time can provide insight on the wettability and is suitable to evaluate the effect of different surface treatments.⁴

Surface Treatment:

Alkaline treatment: wheat straw raw material of two sizes (short length or particulate) were soaked in 3 wt-% NaOH solution at straw/solution mass ratio of 1:2 at room temperature for 24 hours. Hot water treatment was conducted by boiling wheat straw in deionized (DI) water at temperature of 100°C for 2 hours.

Contact Angle Measurement

When a drop of liquid is placed on the surface of a piece of wheat straw, the drop shape changes as time goes because of two mechanisms: spreading or absorption. During the wetting measurement, images of the liquid drop shape were captured and saved. The contact angle was measured on twelve wheat straw surfaces (untreated, NaOH and hot water treated, stem and sheath, and exterior and interior). Measurements made with two liquids: polyester resin (Acrodur DS3530) and DI water at room temperature. Results are shown in Table 1. Each type of sample was measure 6-8 times, and 2-5 locations in each sample were measure. The contact angles were measured on both sides of the droplet and averaged. The first 15 seconds of data points were used to report the initial contact angle for each drop (see Table 1). The wettability associated

with resin type, drop location on the wheat straw surface were compared.

Table 1 initial contact angle measurement results

Straw Part	Surface	Test Media	Initial Contact Angle (°, degree)		
			Untreated	Hot water treated	NaOH treated
Stem	Exterior	DI water	89.8±3.53	89.0±3.71	48.5±4.80
		Acrodur DS3530	82.6±2.45	87.5±3.50	59.4±3.34
	Interior	DI water	24.5±5.92	44.0±4.82	33.9±3.61
		Acrodur DS3530	49.5±2.96	67.6±5.72	45.5±2.35
Sheath	Exterior	DI water	91.0±4.21	92.8±2.43	64.2±6.74
		Acrodur DS3530	81.0±2.79	95.1±1.52	81.5±3.58
	Interior	DI water	88.6±3.25	81.8±2.37	65.9±8.07
		Acrodur DS3530	81.9±2.20	85.8±1.29	74.6±5.62

The straw has a tube-like structure, the exterior surface is the outer surface of the straw whereas the interior surface is the inner part of the tube. Two parts of the straw were investigated: stem (inter-nodal) and sheath (near-nodal). The results of this study showed that the contact angles of the interior surface of the straw were smaller than those on the exterior surface for the same test media on the untreated wheat straw stem. Both Acrodur and DI water had initial contact angles in range of ~82-90° on untreated stem exterior, whereas the contact angles on untreated stem interior are much lower, being 24° for DI water and 49° for Acrodur, respectively. However, both sheath interior and exterior of untreated wheat straw did not show much differences in measured contact angles, which were in range of 80-91° and comparable to those on stem exterior. This demonstrated that the behavior of the stem interior was quite different from those on other three surfaces. This phenomenon can find explanations from their surface chemical compositions and anatomical structure, which conforms to their plant functions of transporting water and nutrients.¹²

After hot water treatment, both Acrodur and DI water contact angles on sheath interior and exterior, and stem exterior changed slightly and remained in the same range as on untreated ones. Surprisingly, hot water treatment increased the contact angles on the stem interior to 44° and 67° for hot water treated and NaOH treated wheat straw, respectively.

NaOH treatment showed significant effect on sheath interior and exterior, and stem exterior. The DI water contact angles dropped to 48° for stem exterior, which was the largest change, and 64°, 65° for sheath interior and exterior. The Acrodur contact angles on these three surfaces dropped significantly too. This indicates that NaOH treatment was an effective method for improving the wettability of wheat straw surfaces. NaOH treatment achieved the same effect on stem interior, whereas the contact angle increase was observed but not as much as the hot water treated did. The optical observation also showed the smooth surface seen on the exterior surface disappears and porous structure appears, this phenomenon is called chemical etching.

Pressboard Manufacturing and Flexural Test

In general, the pressboard production consists of: 1) **size reduction** process to convert straw material in smaller particles or length, followed by 2) **binder addition** and 3) **compression**

molding of the composite material in a confined mold, where chemical or physical changes are initiated by heat and the material solidifies to its final shape. ⁷

Materials

- 1) Wheat straw: air-dried wheat straw was hammer-milled to decrease the size. Two sizes of wheat straw fibers were used in this research. Alkaline and hot water treatments were carried out separately on both sizes, using the procedure described previously.
- 2) Polyester binders: Acrodur DS3530 and mixture of Acrodur DS3530 and nanocellulose. Acrodur is a family of aqueous acrylic resins based on a polycarboxylic acid and a polyalcohol. The working principle of polyester binders is that fibers are impregnated in monomer solution with low viscosity and then these pre-polymers are crosslinked in situ by heat to form a robust 3D network. In composite products, polyester binders are said to deliver a remarkable list of benefits. Firstly, it works for natural fibers, due to its chemistry; and secondly, it cures at relatively low curing temperature and with short heating time; thirdly, the only byproduct of curing is water.

Pressboard Preparation

The production process involves the use of hydraulic press and a custom-designed pressing mold set consisting of a square mold, a flat plate and a solid plunger. The process steps involved in this practice are summarized in Table 2.

Table 2 Summary of steps for pressboard preparation

Step		Parameter or Technique used
1	Size reduction	Milling and screening
2	Resinating	Spray impregnation
3	Drying	Convection oven, at 50°C
4	Mat forming	Hand layup
5	Pre-pressing	At 25,000-45,000lb
6	Hot pressing	At 170-190°C/ aeration

Wheat straw was dried in a convection oven to first remove the moisture to facilitate the wetting process during resination. After formulation, wheat straw was weighed and added to the mixer bowl for impregnation. The DI water diluted polyester solution (50:50) was then sprayed slowly onto the straw while being stirred. The mixer was used to improve the dispersion of resin on straw, allowing better wetting of polyester by spreading over the surface or into the structure of straw. Impregnation was considered effective when resin is evenly distributed on the fiber surface. Once impregnated, the excess water was removed in convection over at 50°C to achieve moisture content of less than 10%.

The hand layup procedure was used to prepare straw-polyester composite mat. The resinated straw was formed into a square fiber mat sized in the mold. Prior to hot pressing, the mold surfaces were covered by Teflon sheets for easy release after pressing. The prepared straw mat was pre-pressed in a cold press at room temperature to reduce the straw mat thickness and volume. The compression molding cycle times of a few minutes were possible at process temperatures of above 150°C. The fiber mat was then placed into the hydraulic press and compressed into its final shape and thickness. The increased temperature cured the polyester

resin and caused a series of physical and chemical changes, which consolidated and hardened the final product. Depending on selected press parameters, various thicknesses and densities of the pressboards were produced. At last the composite pressboard was removed from the mold. Both residual and produced water was vaporized during the heating stage. So a de-gassing time during hot pressing was necessary to release entrained steam and air to avoid delamination of the pressboard. After removing from the mold and cooling down, the finished composite pressboards were cut into testing specimens using a saw blade for mechanical test.

Flexural Test

The flexural properties of pressboards were measured by three point loading system, according to ASTM D790. A sample bar with rectangular cross section rested on two supports, and loading was applied to a third point, located at the midpoint on the top. The specimen was deflected until rupture occurred or until a maximum strain of 5.0% was reached, whichever occurred first.¹³

The results are summarized in Tables 3-6. Two types of straw were used: wheat straw #1, which was cut in length <3cm; and wheat straw #2, which was a particulate prepared by hammer mill.

Table 3: Hot press condition: F=30,000lb, T=170°C, time=10min

Treatment	Wheat straw	Acrodur DS3530	Flexural Strength (MPa)	Flexural Modulus (MPa)
Untreated	#1	20%	12.4	2562
Untreated	#1	40%	17.6	1642
Untreated	#2	20%	13.2	2622
Untreated	#2	40%	21.4	3128

Table 4: Hot press condition: F=30,000lb, T=170°C, time=10min

Treatment	Wheat Straw	Acrodur DS3530 -nanocellulose	Flexural Strength (MPa)	Flexural Modulus (MPa)
Untreated	#1	20%	5.3	1197
Untreated	#1	40%	10.5	1814
Untreated	#2	20%	5.3	1120
Untreated	#2	40%	25.7	2892

Table 5: Hot press condition: F=45,000lb, T=170°C, time=10min

Treatment	Wheat Straw	Acrodur DS3530	Flexural Strength (MPa)	Flexural Modulus (MPa)
Untreated	#1	20%	34.5	5789
Untreated	#1	40%	36.3	5694
Untreated	#2	20%	36.2	6092
Untreated	#2	40%	34.9	5723

Hot water	#1	20%	36.9	4917
Hot water	#1	40%	32.8	3835
Hot water	#2	20%	39.6	6767
Hot water	#2	40%	37.2	5482
NaOH	#1	20%	16.5	3121
NaOH	#1	40%	27.2	3444
NaOH	#2	20%	16.9	4004
NaOH	#2	40%	39.7	6876

Table 6: Hot press condition: F=45,000lb, T=170°C, time=10min

Treatment	Wheat straw	Acrodur DS3530 -nanocellulose	Flexural Strength (MPa)	Flexural Modulus (MPa)
Untreated	#1	20%	33.4	6236
Untreated	#1	40%	35.8	5950
Untreated	#2	20%	37.1	6239
Untreated	#2	40%	49.1	9083
Hot water	#1	20%	30.8	5545
Hot water	#1	40%	30.7	4874
Hot water	#2	20%	32.8	6473
Hot water	#2	40%	38.7	5582
NaOH	#1	20%	19.4	3759
NaOH	#1	40%	36.5	5986
NaOH	#2	20%	19.1	4270
NaOH	#2	40%	41.4	6656

The production process was carried out with materials formulations and hot pressing conditions as parameters. The properties of final products are the overall reflection of these parameters. In this section, the relationships of processing parameters and mechanical property are discussed and evaluated. Several formulations of straw and binders were tested, where two straw sizes were used. The polyester resin was Acrodur DS3530 or mixture of Acrodur DS3530 and nanocellulose fiber (prepared mechanically with refiners using Eucalyptus pulp). The processing parameters including molding temperature (T), pressure (P), and resident time (t), have significant influences on the mechanical performance of the resultant pressboards. In compression molding, temperature and time together will affect the fiber degradation. Pressure will affect the density and thickness. Mechanical properties are the reflection of the changes of board density and resin content.

The following observations can be made: 1) the pressboards made at 30,000lb exhibited lower flexural strength and modulus than those prepared at 40,000lb; 2) the pressboards made with higher binder content were had higher flexural strength and modulus; 3) the pressboards made from straw fiber were not as strong as those made from straw particulate (powder-like prepared

using mill); 4) the surface treatments did not show positive evidences that better wettability necessarily leads to improved mechanical property; 5) the pressboards made with mixture of Acrodur DS 3530 and nanocellulose as binder were superior to those made with Acrodur DS3530. Overall the best result was at 49.9 MPa for flexural strength and 9083 MPa for flexural modulus, which was from the board made with untreated wheat straw particulate, and 40% Acrodur/nanocellulose mixture, compressed at 40,000lb and 170°C for 10 minutes.

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Bibliography

1. Koronis, G., Silva, A. & Fontul, M. Green composites: A review of adequate materials for automotive applications. *Compos. Part B Eng.* **44**, 120–127 (2013).
2. Bismarck, A., Mishra, S. & Lampke, T. Plant Fibers as Reinforcement for Green Composites. in *Natural Fibers, Biopolymers, and Biocomposites* (CRC Press, 2005). doi:doi:10.1201/9780203508206.ch2
3. Shankar, R. S. Srinivasan, SA. Shankar, S. Rajasekar, R. Kumar, RN. Kumar, PS. Review article on wheat flour/wheat bran/wheat husk based bio composites. **4**, 1–9 (2014).
4. Shi, S. Q. & Gardner, D. J. Dynamic Adhesive Wettability of Wood. *Wood Fiber Sci.* **33**, 58–68 (2001).
5. Halvarsson, S., Edlund, H. & Norgren, M. Properties of medium-density fibreboard (MDF) based on wheat straw and melamine modified urea formaldehyde (UMF) resin. *Ind. Crops Prod.* **28**, 37–46 (2008).
6. Godavarti, S. Thermoplastic Wood Fiber Composites. *Nat. Fibers, Biopolym. Biocomposites* (2005). doi:doi:10.1201/9780203508206.ch10
7. Halvarsson, S. *Manufacture of straw mdf and fibreboards*. (2010).
8. Medina, L., Schledjewski, R. & Schlarb, A. K. Process related mechanical properties of press molded natural fiber reinforced polymers. *Spec. Issue 12th Eur. Conf. Compos. Mater. ECCM 2006* **69**, 1404–1411 (2008).
9. Yasin, M., Bhutto, A. W., Bazmi, A. A. & Karim, S. Efficient utilization of rice-wheat straw to produce value-added composite products. *Int. J. Chem. Environ. Eng.* **1**, 136–143 (2010).
10. Franco, P. H. & Valadez-González, A. Fiber-Matrix Adhesion in Natural Fiber Composites. in *Natural Fibers, Biopolymers, and Biocomposites* (CRC Press, 2005). doi:doi:10.1201/9780203508206.ch6
11. Halvarsson, S., Edlund, H. & Norgren, M. Wheat Straw As Raw Material for Manufacture of Straw Mdf. *BioResources* **5**, 1215–1231 (2010).
12. White, N. M. & Ansell, M. P. Straw-reinforced polyester composites. *J. Mater. Sci.* **18**, 1549–1556 (1983).
13. Specimens, P. & Materials, E. I. Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials 1. *Annu. B. ASTM Stand.* 1–11 (2011). doi:10.1520/D0790-10.