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Advanced Binderless Board-like Green nanocomposites from Undebarked Cotton Stalks, and Mechanism of Self Bonding

By

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ABSTRACT

Self-bonding of air dry undebarked cotton stalks during hot pressing in a closely fitting mold was studied. Advanced board like green nanocomposites from ground undebarked cotton stalks were introduced, for the first time, in the present work. The dry forming process was adopted. Moderate molding pressure and temperature were selected and applied in a tight die. Thus saving water, energy, and avoiding the use of any binders; to achieve an environment friendly green product. Green Nanocomposites having densities in the range 1.27-1.29 g/c.c. as well as 1.03-1.06 g/c.c. were prepared. It was found that particle size, and cell wall morphological structure play a great role in self bonding. Properties of composites prepared from the fine fraction of cotton stalks were superior to those prepared from cotton stalks coarse fraction at same conditions. This is attributed - among other things - to the dominance of pith (parenchyma cells) in the fine fraction. Such cells possess a high lumen to cell wall ratio, which renders them more deformable under pressure leading to more intercellular or interparticle bonding. Advanced Binderless Green Nanocomposites having bending strength as high as 637 Kg/cm² and water absorption as low as 12.1% were obtained from the ground undebarked cotton stalks. The results show clearly that the advanced green nanocomposite obtained by dry forming process, without addition of any binders, is superior to hardboard obtained from cotton stalks by the conventional wet web formation process. The mechanism of self-bonding was discussed.

Keywords: Binderless Board; Self-Bonding; Undebarked Cotton Stalks
1. INTRODUCTION AND OBJECT:

In contradistinction to other agricultural residues, cotton stalks are comparable to most common species of hard woods [1]. However, the investigations indicated that undebarked cotton stalks are unsuitable for the production of fine paper and dissolving pulps [2, 3]. Debarking improves the suitability of cotton stalks for pulp and paper; but it is a difficult (unfeasible) mechanical task to debark one-year-old plants. A successful approach introduced undebarked cotton stalks for newsprint making [4]. The suitability of cotton stalks for production of charcoal, fuels, tars, and oils were studied in a series of articles e.g. [5, 6].

Earlier work on hardboard and particle board from agricultural residues - including cotton stalks- showed that a drastic drawback is the very high water absorption and thickness swelling (deteriorated dimensional stability) of the obtained boards [7-11]. This necessitates the addition of higher amounts of resins in order to obtain boards comparable to those obtained from wood wastes. These facts make it clear that board making from cotton stalks and other agricultural residues is still not satisfactory and needs further research.

The present paper aims at investigating the suitability of undebarked cotton stalks for producing binderless lignocellulose composite by using the dry forming process under moderate pressure and temperature. Self bonding mechanism in this case is also under consideration.
2. EXPERIMENTAL

2.1. Raw Material:

Egyptian undebarked cotton stalks were used in this work. The physical and chemical analyses were done according to TAPPI procedures and German Standard Methods. The undebarked cotton stalks were ground in a Wiley mill, and sieved rejecting the fraction > 1.0 mm. The moisture content of the air dry ground undebarked cotton stalks amounted to about 7%. To increase this moisture, the ground cotton stalks was put in a desiccators containing NaCl or KCl saturated solution for 2-4 days, depending upon the desired moisture increase. This was done to study the influence of increasing the initial moisture content of the cotton stalks particles.

2.2. Preparation of lignocellulose Composite without using any binders:

The dry forming process was used in this work for preparation of hardboard-like composite of about 4mm thickness. The details are as follows:-

A closed stainless steel die was designed which enabled obtaining 3 test specimens, each of 11cm long and 2.2 cm width, together in each experiment. The calculated amount (depending on the desired thickness and density) of ground cotton stalks was carefully filled in the die, and prepressed by hand press if necessary. The die containing the cotton stalks was then transferred to a hydraulic press which was heated before pressing to the desired temperature. The desired pressure was applied and the die containing the samples was left for 7 minutes under continuous pressure at the maximum temperature of 160 ºC. It took from 8-10 minutes until the die containing the samples reach the maximum temperature. At the end of the reaction time, the press was cooled by cold water until the
temperature of the press and respectively the die reaches 20°C. Thereafter the pressure was released and the cold die opened. The prepared board-like composite made in this work, by the dry forming process mentioned above, are designated binderless lignocellulose green nanocomposite to differentiate them from hardboards prepared by the conventional wet web forming process in presence of resins added as binders.

2.3. Testing of the prepared composite: Before testing the composite, samples were conditioned at 60 % R.H. and 20°C for one week.

Bending strength of the composites:

The testing machine used was WAM Rauenstein Universal Testing Type. The bending strength was obtained as follows:

\[
\text{Bending Strength} = \frac{3PL_s}{2ba^2}
\]

Where \( P \) = force at fracture of test specimen; \( L_s \) = bearing distance between supports; \( b \) = width of test specimen; \( a \) = thickness of test specimen.

Water absorption and thickness swelling: was determined according to ASTM D-1037 except that a test specimen of 5 cm long and 2.2 cm width was used in the present work.

Moisture content of samples: Samples were weighed, oven dried at 105°C till constant weight, and moisture percentage was calculated.

Densities of the samples were determined as follows:

\[
\text{Density} = \frac{\text{oven dry weight (g)}}{\text{sample volume (cm}^3\text{)}}
\]
RESULTS AND DISCUSSION

3.1. Self Bonding Mechanism:

In the usual method of fiberboard making, a lot of water is used during the formation of the wet web. Besides, addition of resins is essential to obtain fiberboard having satisfactory properties. The dry forming process was the subject of intensive investigation because it saves water and binders, resulting in green environment friendly products [12, 13]. In this process fiber bonding respectively particle bonding during binderless lignocellulose composite making is attributed to both physical and chemical changes. The chemical changes take place in two stages. The first stage is a hydrolysis stage, whereby acetic and formic acids and some sugars are liberated through the moisture found in the wood particles and then these acids hydrolyze the hemicellulose in the lignocellulosic material. The moisture content loss during sample processing must be attributed to hydrolysis reactions; since escaping of water vapor from the closely fitting die is most unlikely. Some of the pentoses and hexoses, produced during hydrolysis, are further dehydrated to furfural and hydroxymethyl furfural respectively. Also, the lignin becomes activated i.e. a part of the lignin-carbohydrate bond becomes cleaved (cracked by the formed acids) resulting in the exposition of new functional groups or sites. The second reaction stage, which seems to take place at a slower rate than hydrolysis, is the recondensation of the activated lignin molecules as well as lignin degradation products (such as phenol, which might be formed at high temperature more than 155°C) with furfural. Consequently, the use of a closed die for preparing the binderless composite was recommended; in order that the volatile substances do not
escape, namely formic acid, acetic acid, and furfural (of boiling points 100.8°C, 119°C, and 162°C respectively) [8-16]. In this way the volatile substances are fully made use of for bonding the fibers, and binders can be completely dispensed with. Moreover, sugars liberated during the hydrolysis stage are incorporated into the natural nanoporous structure of the lignocellulosic material cell walls [17-23]; leading to more interparticle bond formation. Thus, advanced binderless green nanocomposites of superior properties were obtained under mild conditions.

3.2. Properties of binderless lignocellulose green nanocomposite composite from undebarked cotton stalks:

The chemical composition of undebarked cotton stalks was determined as mentioned in the experimental section and is shown in Table 1. The undebarked cotton stalks were ground in a Wiley mill and sieved to possess particle size not more than 1 mm. The ground stalks were fractionated into a fine fraction and a coarse fraction. The coarse fraction possessed particle size of 1.0-0.5 mm and consisted mainly of the woody fraction of the cotton stalks and bast fibers from the bark. The fine fraction possessed particle size of 0.5-0.1 mm and contained most of the pith (parenchyma cells) present in the cotton stalks which in the present work amounted to about 15% based on undebarked stalks [1-4].

From the preliminary experiments, it was found that a temperature of 160°C was the most suitable for preparation of binderless lignocellulose composite from undebarked cotton stalks. Accordingly, molding temperature in all experiments was 160°C. Binderless lignocellulose green nanocomposites were prepared from the ground cotton stalks using a closed die and dry forming process as mentioned in the
3.2.1. **Experiments on coarse fraction of the undecked cotton stalks:**

In these experiments, composites (board-like) were prepared from ground cotton stalks of particle size 1-0.5 mm, without adding any binders.

**Table 2** shows the properties of composites obtained in case of using low as well as moderate molding pressures.

The composite samples prepared by using low molding pressure of 50 Kg/cm$^2$ possessed density in the range 1.03-1.06 g/c.c. The thickness of these composites was about 4 mm. It is clear from **Table 2**, in case of using low molding pressure, that increasing the initial moisture content from about 7% to 10% and 13% resulted in continual increase in bending strength and water resistance of the obtained composites.

The densities of the composite samples prepared from cotton stalks coarse fraction by using a moderate molding pressure of 100 Kg/cm$^2$ lay in the range 1.27-1.29 g/c.c., and the thickness was about 4 mm. It is evident from **Table 2** that increasing the molding pressure improved much the properties of the obtained composite. Composites having bending strength as high as 598 Kg/cm$^2$ and water absorption as low as 12% were obtained. The optimum initial moisture content of the ground undecked cotton stalks was found to be between 10 and 13%.

It is worth mentioning that all composite samples obtained from undecked cotton stalks by the dry forming process, in the present work, without adding any binders are superior to the cotton stalks hardboard (made by wet web formation
process) containing up to 2% phenol formaldehyde (based on pulp) as binder. Moreover, in the wet web formation process, about 15-20% of the raw material is lost during pulping and beating of the cotton stalks to enable formation of the wet web [7, 8].

3.2.2. Experiments on fine fraction of the undebarked cotton stalks:

In these experiments, composite was prepared from ground undebarked cotton stalks of particle size 0.5 - 0.1 mm without adding any binders. The results are given in Table 3.

The composite samples prepared by using low molding pressure possessed densities in the range 1.03 - 1.06 g/c.c.; while those prepared under moderate pressure possessed densities of 1.27-1.29 g/c.c. Thickness of composite in both cases was about 4 mm.

At molding pressure of 50 Kg/cm², raising the initial moisture content increased the bending strength and water resistance of the obtained composites as shown in Table 3. When molding pressure of 100 Kg/cm² was used, increasing the initial moisture content from about 7% to 10% and further to 13%, resulted in slight increase in the bending strength; and the water resistance of the obtained composite was some what better.

In other words, increasing initial moisture content -contrary to the case of coarse fraction- did not much improve properties of composite. Accordingly the self bonding here might be mainly due to the good thermoplastic flow behavior of the pith cells dominant in the fine fraction of cotton stalks. We have shown before [12] that pith cells, because it possess a high lumen/cell wall ratio, render themselves more deformable under pressure and thus could pack closer together and conform better resulting in a more intercellular or interparticle bonding. On the other hand, in the case of cotton stalk coarse
fraction which is mainly consisted of woody particles and bast fibers, it was essential to increase the initial moisture content up to 10 or 13% depending upon pressure to improve plasticization and enhance the hydrolysis reaction which is here the main factor for self bonding.

The present work showed that properties of lignocellulose composite prepared from cotton stalks fine fraction is much better than those prepared from cotton stalks coarse fraction at same conditions. This is attributed -among other things- to the presence of pith (parenchyma cells) in the cotton stalks fine fraction. Accordingly, it can be concluded that in binderless lignocellulose composite the nature of cell wall morphological structure plays a great role in self bonding.

**Conclusion:**

Plastic-like products of good strength and water resistance are obtained from ground undebarked cotton stalks by applying a moderate molding pressure and temperature in a tight die. A minimum water must be present in the cell walls. Experiments with an oven–dry material failed to give products of any strength. The coarse fraction requires higher initial moisture content than the fine fraction (which contains pith) to get optimum results. The extent of interparticle bond formation depends on morphological, chemical, and colloidal properties of the lignocellulusic material -as well as- on the processing conditions. A decisive factor is the thermoplastisity developed under pressure and heat.
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### Table 1

Chemical composition of ground undebarked cotton stalks

| Particle size     | Unfractionated less than 1 mm | Coarse Fraction 1-0.5 mm | Fine Fraction 0.5-0.1 mm |
|-------------------|-------------------------------|--------------------------|--------------------------|
| Lignin%           | 22.1                          | 23.2                     | 21.1                     |
| Pentosans%        | 18.2                          | 18.1                     | 18.3                     |
| Alphacellulose %  | 43.9                          | 45.1                     | 43.3                     |
| Ash%              | 4.8                           | 3.7                      | 5.4                      |
| **Properties of binderless lignocelulose green nanocomposite from undebarked cotton stalks coarse fraction** |
|---|
| **Particle size** | 1-0.5 mm |
| **Molding temperature** | 160 °C |
| **Molding pressure kg/cm²** | 50 | 100 |
| **Initial moisture %** | 7.2 | 10.2 | 13.1 | 7.2 | 10.2 | 13.1 |
| **Moisture after Pressing %** | 7.1 | 7.4 | 7.6 | 7.1 | 7.5 | 7.7 |
| **Bending strength kg/cm²** | 270 | 285 | 327 | 480 | 596 | 598 |
| **Water Absorption %** | | | | | | |
| After 1 hour | 12.2 | 12.1 | 11.1 | 3.6 | 2.3 | 2.2 |
| After 24 hours | 35.6 | 31.3 | 26.5 | 14.2 | 12.5 | 12.3 |
| **Thickness Swelling %** | | | | | | |
| After 1 hour | 4.6 | 3.3 | 3.2 | 3.2 | 2.5 | 2.2 |
| After 24 hours | 22.5 | 12.1 | 12.1 | 12.4 | 9.6 | 9.9 |
|                                |                  |                  |                  |                  |                  |
|--------------------------------|------------------|------------------|------------------|------------------|------------------|
| **Table 3**                    |                  |                  |                  |                  |                  |
| **Properties of binderless lignocelulose green nanocomposite from** |                  |                  |                  |                  |                  |
| **Undebarked cotton stalks fine fraction** |                  |                  |                  |                  |                  |
|                                |                  |                  |                  |                  |                  |
| Particle size                  | 0.5-0.1 mm       |                  |                  |                  |                  |
| Molding temperature            | 160 ºC           |                  |                  |                  |                  |
| Molding pressure kg/cm²        |                  | 50               | 100              |                  |                  |
| Initial moisture %             | 7.1              | 10.2             | 13.1             | 7.1              | 10.2             | 13.1             |
| Moisture after Pressing %      | 6.7              | 7.4              | 8.1              | 7.2              | 7.5              | 8.1              |
| Bending strength kg/cm²        | 344              | 491              | 528              | 620              | 635              | 637              |
| Water Absorption %             |                  |                  |                  |                  |                  |
| After 1 hour                   | 13.5             | 10.1             | 11.6             | 2.2              | 2.6              | 3.1              |
| After 24 hours                 | 36.3             | 20.4             | 22.1             | 12.5             | 13.2             | 12.9             |
| Thickness Swelling %           |                  |                  |                  |                  |                  |
| After 1 hour                   | 11.6             | 11.5             | 12.1             | 1.3              | 1.5              | 1.6              |
| After 24 hours                 | 24.5             | 21.7             | 22.1             | 9.8              | 10.3             | 9.9              |