

HEAT APPLIED CHITOSAN TREATMENT ON HARDWOOD CHIPS TO IMPROVE PHYSICAL AND MECHANICAL PROPERTIES OF PARTICLEBOARD

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High-heat treatment after surface application of chitosan was used in an effort to improve physical and mechanical performances of particleboard. Particleboard is mainly used in the furniture industry and also used as a home decoration material; however, it has a poor dimensional stability. In this work, hardwood chips were obtained from a commercial plant; half of the chips were used for the control panels without chitosan treatment, and the other half were treated with chitosan acetate solutions (2% wt). Those chitosan-treated particles were also exposed to extra high-heat (140°C) treatment for 90 minutes to convert chitosan acetate back to chitin. Liquid phenol-formaldehyde resin was sprayed onto dry particles at a level of 6 and 7% (wt) based upon oven-dry weight. The mat was pressed (200°C) for 11 minutes to form 19 mm thickness and a target of 0.63 g cm⁻³ density panels. Thickness swelling, linear expansion, and water gain of the treated panels were reduced over untreated panels during a 24-hour water-soak test. In addition, chitosan-treated panels showed better internal bond strength than control panels. Static bending test results showed a negative effect for the chitosan treated particleboard.

Keywords: Particleboard; Chitosan; Dimensional stability; Chitin

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INTRODUCTION

Particleboard is a reconstructed woodbased material that is composed of wood particles bonded together with synthetic resin under heat and pressure in a hot press. Particleboard is usually used for interior applications such as home decoration and furniture; however, sometimes these panels can be damaged when exposed to water, such as in kitchen and bathroom applications.

Wood is a hygroscopic material that swells as it absorbs/adsorbs moisture and shrinks as it loses moisture below the fiber saturation point. Such dimensional changes are different in the case of reconstituted wood products, such as fiberboard and particleboard, relative to solid wood products. For example, thickness swelling of flakeboard when exposed to moisture is greater than would be expected from the normal shrinking and swelling of the component wood flakes. In addition to the swelling, water contact, or high relative humidity can greatly affect the state of stress that exists in the material. The in-plane movements can cause high internal stresses due to the restraint by

metal fasteners. These stresses may be large enough to cause buckled panels, pushed out nails, and separation of the panel from the structure.

Dimensional stability of wood-based panels can be affected by most process variables such as wood-furnish, flake size and geometry, resin level and type, and pressing conditions. Improved dimensional stability should be possible through a better understanding of these variables as well as by special treatments such as chemical modifications, steam and heat treatments, and special coatings. Dimensional stability of particleboard can be improved permanently with chemical modifications (such as, with acetylation to alter the wood matrix by replacing the polar hydroxyl groups with bulkier, less hydrophilic acetate groups). Rowell *et al.* (1986) and Youngquist *et al.* (1986) studied acetylation of flakes and reported substantial reductions in thickness swelling and water gain.

Resin impregnation, heat, and steam treatments have been used to improve the dimensional stability of particleboard and waferboard. These treatments were effective; unfortunately they were costly or reduced the mechanical properties of the panels (Haygreen and Gertjens 1972; Geibeler 1983). Improving the dimensional stability of woodbased panels should not be a goal in itself to the extent that the other properties of the panels, such as strength and stiffness, are adversely affected or the product becomes prohibitively expensive.

Chitosan is a modified carbohydrate polymer derived from chitin, one of the most abundant polysaccharides in nature, by deacetylation. Chitin is present in crustacean shells, insect exoskeletons, fungal cell walls, microfauna, and plankton. Chitosan is a polysaccharide formed primarily of repeating units of beta (1-4) 2-amino-2-deoxy-D-glucose (or D-glucosamine). Generally, about 70 to 90% of the units are deacetylated, with 10 to 20% remaining acetylated (Sandford 1988).

Today, chitosan is used widely in medical, health, waste management, and agricultural areas. Although chitosan films, even when not dissolved, are more or less swollen by water, the amount of swelling is reduced by heating, formaldehyde treatment, or acetylation, which produces chitin again. Chitosan is used as a paper sizing or additive to improve paper mechanical properties and water resistance. Moreover, it has been used for improving water resistance of the textile, wool, and bonding properties for tobacco and solid wood (Muzzarelli 1977).

In this study the most abundant two materials in nature, cellulose and chitin, are combined together to achieve an enhanced material. Chitosan was applied as a chitosan acetate solution onto hardwood chips. Later, with help of high-heat treatment, it was converted to a chitin again to achieve dimensional stability for particleboard without compromising mechanical properties. In humid environments and during transportations and also in handling process, particleboard should be protected from water.

With chitosan treatment, particleboard is a much better material to use in those environments, and its organic nature makes chitosan safe and environmentally friendly. In nature, a covering of chitin protects some insects and fruits from environmental hazards; in this research, that approach is appropriated onto wood particles in order to protect them from water damage.

EXPERIMENTAL

Materials

Materials used in this experiment were purchased from industrial companies. Industrial chitosan was used in its powder form, containing crab and shrimp product, and it was purchased from Vanson Corporation, Redmond, WA. This product has a 73% degree of deacetylation and 500 cps viscosity. The wood particles used in this study were obtained from a commercial particleboard plant, Allegheny particleboard, Kane Pennsylvania, USA. Furnish particles consisted of local hardwood species such as maple. Surface layers chips were fine particles around 1 mm sizes. Core layer chips were shaving particles with 2 to 5 mm width and the same thickness due to cutting techniques. As a bonding adhesive, liquid phenol formaldehyde resins were chosen instead of urea formaldehyde resins due to researcher preliminary work and were obtained from Borden Chemical Company. Cascophen IN-703A with resin solid content 53%, viscosity 150 cps, and a pH of 10 to 11 was used for board face layers. Similarly, Cascophen IN-303K with a resin solid content 51%, viscosity 200 cps, and a pH of 12 was used for the core layer.

Treatments

Chitosan treatment

A 2% solid content was chosen for this work based on preliminary work by the authors, some literature data (Basturk and Guntekin 2009; Umemura *et al.* 2009), and also due to viscosity problems of chitosan. Forty grams of chitosan were added to 2 L of 3% aqueous acetic acid solution (60 mL glacial acetic acid added to 2000 mL distilled water) to obtain 2% (wt) chitosan acetate solutions. These aqueous mixtures, pH 4.5, were stirred vigorously at a temperature of *ca.* 60°C for two hours. Dissolved chitosan solutions were cooled to 20°C and stored in closed glass bottles until wood-particle treatment. For the treatment, face and core particles were sprayed with prepared 2% chitosan acetate solutions. The sprayed solutions were applied based on oven-dry weight of wood to get 2% chitosan solid content onto wood particles. After the spray, the treated wood particles were mixed in order to get an even percentage of solution and then they were allowed to air dry.

High-heat treatment

Later, those chitosan-treated and air-dried wood chips were put in an oven for heat treatment to convert chitosan acetate to chitin again. Treated particles were kept for 90 minutes in an oven. The temperature was raised from 90° to 140°C during 15 minutes and then kept at that level. Later, heat-treated chitin covered wood particles were placed in sealable plastic bags to prevent moisture intake before the board assembly.

Board Processing

Particleboards were made in the laboratory. Treated and untreated wood particles (for the control panels) were placed in an oven (95°C) to adjust the moisture content to 3% before resin application. No wax emulsion was used during this experiment. Liquid phenol formaldehyde solutions, as follows, were sprayed onto wood particles. In the case

of board face layers, a 7% solution of Cascophen IN-703A was used. In the case of the core layer a 6% solution of Cascophen IN-303K was used. The furnish-mat was established by hand, and the size of the panel was 50 x 50 cm.

Three-layer boards were made in which the face layers each comprised 36% of the board, and core layer comprised 64%. Then, they were pressed at 200°C for 11 minutes within 1 minute closing time and 2 minutes breathing time. Target density established as a 0.63 gr cm⁻³ with 1.9 cm thickness which was established by steel bars stop. The press was a 300-ton capacity single opening hot-press assembly, Frisch hydraulic press, model 0854. Panels were cooled down after the assembly and stored one week before test samples preparation.

Physical Tests

A water soak test was conducted for determination of physical performances of the particleboards. Test samples were cut 15 by 15 cm and conditioned at 20°C and 50% relative humidity (RH). The thickness was measured to the nearest 0.001 mm with a micrometer at four point's midway along each side, 2.5 cm from the edge of the specimens and averaged for the thickness swelling determination. Then they were submerged horizontally under 3 cm of distilled water maintained at a temperature of 20±1°C. The measurements of samples weight and thickness were taken during a 24 hours period.

Generally, linear expansion (LE) is measured in a humid environment, but in this study, due to difficulty of sample gathering because of chitosan treatment, measurements were taken in a water-soaked environment. This test was simulated from Canadian standards (CSA 0437 Series-93) and adapted to the water soak test. The same specimens measured for thickness swell and water gain also used for linear expansion and linear expansion was measured in both principal directions to the nearest 0.001 mm with a micrometer.

Mechanical Tests

The static bending test, a simply supported center load static bending test, was performed for determination of the bending modulus of rupture (MOR) and bending modulus of elasticity (MOE) on specimens. The specimens (1.7 by 7.6 by 47 cm) were tested with a span of 41 cm. A computer controlled Instron Fatigue Testing Machine, model 1335, and was used with the load-head having a radius of 1.5 times of thickness and moving at a uniform rate of 0.2 cm per minute. Particleboard samples were conditioned at 65% RH and 20°C prior to testing. Also, coupons were taken from these specimens to calculate the density and moisture content of the panels after the bending test.

Specimens of 5 x 5 cm were used for the determination of the internal bond (IB) strength. Samples were conditioned at 65% RH and 20°C in an Aminco-Aire relative humidity chamber for one week prior to testing. Each sample was bonded to a pair of 5 x 5 cm aluminum blocks with hot melt glue. A Riehle Universal Testing Machine was used to apply the load at a uniform-crosshead motion-rate of 0.1 cm per minute. All tests and data analyses were performed according to ASTM D 1037-96a, and some adjustments were made regarding of specimen sizes due to small panel sizes.

RESULTS AND DISCUSSION

Physical Performances

Physical properties of treated particleboard improved with high-heat treatment with chitosan acetate. Chitosan treatment reduced the thickness swelling (TS) of the treated panels over untreated control board (Fig. 1). The thickness swelling of the chitosan-treated panels was reduced on average 38% and 23%, after 2 hours and 24 hours, respectively, compared to control panels.

Chitosan treatment also reduced water gain (WG) of the treated panels by the encapsulating barrier effect. The water absorption of the chitosan-treated panels was reduced on average 48% and 22%, after 2 h and 24 h, respectively, compared to control panels (Fig. 2).

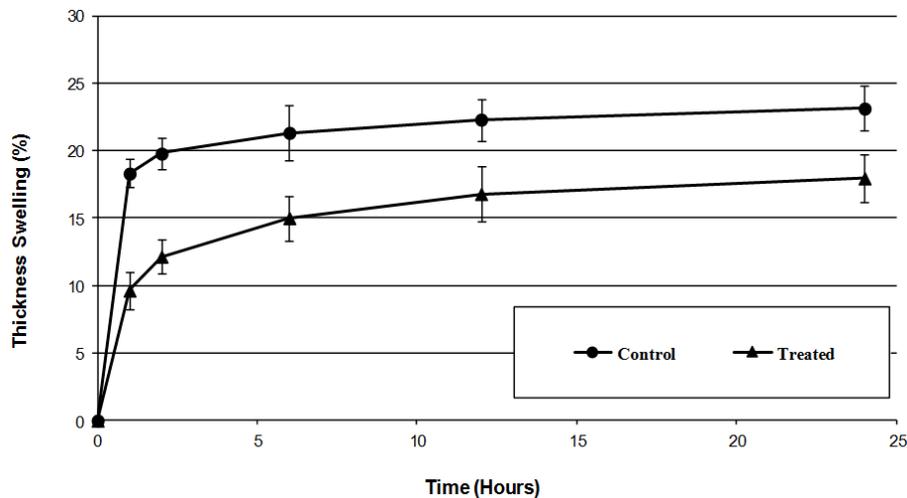


Fig. 1. Thickness swelling percentage of the panels during 24-hour water soak test

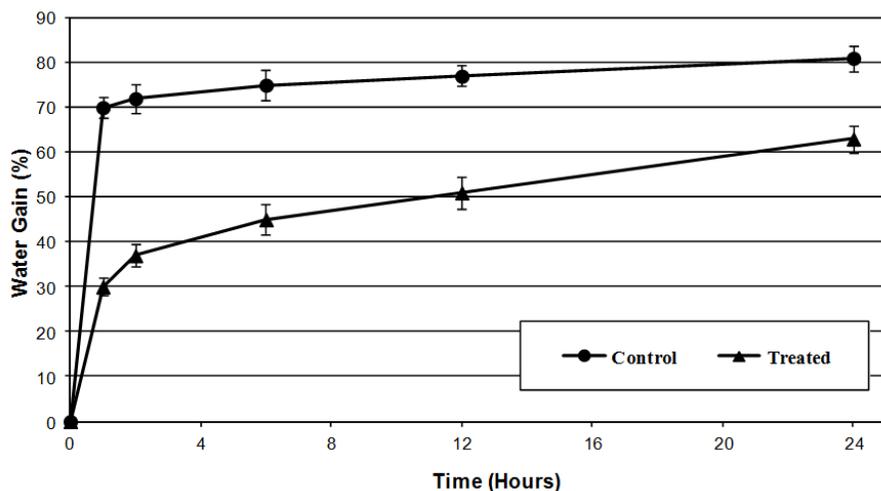


Fig. 2. Water gain percentage of the panels during 24-hour water soak test

Linear expansion, in water-soak, test data in Fig. 3 shows that chitosan treatment worked effectively and reduced the linear expansion resulting from 24 hours of water-soaking by 35% compared to that of the untreated particleboard. This reduction was similar to and better than thickness swell and water gain reductions too. Unfortunately, linear expansion in humid environment could not be performed due to difficulty of chitosan treatment in this study.

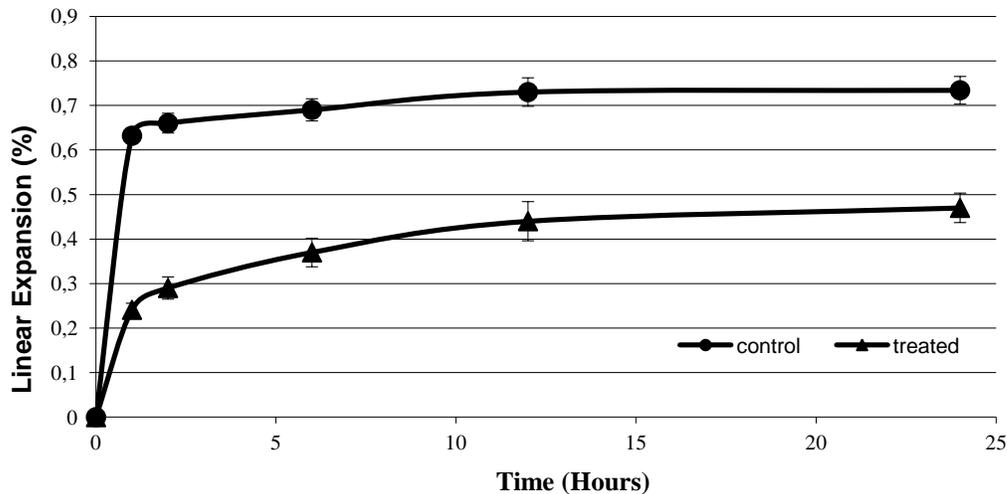


Fig. 3. Linear expansion percentage of the panels during 24-hour water soak test

The improved dimensional stability of the particleboard panels is attributed to a chitin film encapsulating the wood particles and blocking some of the cellulose hydrophilic hydroxyl groups at the chitin/cellulose interface. Water-soluble chitosan acetate over the wood particles is converted to water-insoluble chitin by high-heat application and also hot-pressing. This chitin acted as a water barrier layer on the wood particles and this significantly reduced the thickness swelling of the chitosan-treated panels. This same effect was observed in other situations: an anti-shrinking effect of chitosan for wool (Masri *et al.* 1986) and lack of water penetration in chitosan-treated wood samples in an aqueous alkaline environment. Also, as stated by Basturk and Guntekin (2009), heat treatment after application of chitosan improved TS and WG values.

As reported by Umemura *et al.* (2005), chitosan and wood have polycationic and polyanionic natures, respectively. Thus, a certain affinity would be expected and intermolecular interactions would take place between them. In addition, chitosan is basically insoluble in water, which contributes to its good bonding property. This can explain the good dimensional stability of the hardwood particleboard.

Corroborating this study, Ohmori *et al.* (1998) reported that chitosan treatment of a wood surface helped improve the dry bond strength and water resistance of UF resin and polyvinyl acetate resin adhesives.

Strong correlations were also observed among LE, TS, and WG reductions of chitosan-treated panels. After the 2-hour and 24-hour water soak test, LE, TS, and WG

reductions were almost identical to each other, and this supports the barrier theory. After the 24-hour water soak, water gain was low; on the other hand, thickness swelling after 24 hours was still around 30%, and this also shows that covering materials with chitin aids dimensional stabilization. However, chitosan application onto wood particles could not achieve a continuous chitosan film, so that is not a perfect capsulation. Therefore, TS, LE, and WG reductions showed diminishing reductions during a 24-hour water soak. Also, chitin, which behaves like a thermoset material (Toffey *et al.* 1996) mechanically restrains panel thickness swelling, and therefore reduces thickness swelling of the chitosan treated panels. In use, particleboards typically are exposed to water for a short period of time; therefore, this chitosan application should be sufficient enough to protect the wood materials in most instances.

Mechanical Performances

Mechanical properties of particleboard were affected differently by high-heat applied chitosan treatment. In case of static bending test results, modulus of rupture and modulus of elasticity were affected negatively and showed an average of 12% and 16% reduction compared to control panels due to high-heat chitosan treatment (Table 1). Those reductions could be caused by high-heat treatment of chitosan applied on wood particles; more than one hour and 140°C heat can cause some reductions due to wood structure. In fact, long-time high-heat negatively affects and reduces the wood bending strength and stiffness.

The results are shown in Table 1. Compared with the untreated samples, chitosan treatment resulted in an increase in the internal bond strength. Improvement of internal bond strength was almost double that of the control boards. One possible explanation is that a chitin layer could be barricading the adhesive from soaking inside the wood particles; hence more adhesive stayed onto wood chips, which increased the internal bond strength of the treated panels. This kind of behavior, adhesive staying on wood particles is very desirable for the particleboard production. Also, a chitin barrier could have delayed the cooling of the panels, and that extra heat resulted in better IB results. In case of the internal bond strength, there was no negative effect of the high-heat application.

Density and moisture content values were calculated from coupons taken from used bending test specimens. Average density of the control panels was around 0.64 gr cm⁻³, and the average density of the treated panels was around 0.65 gr cm⁻³. These density values should not affect the bending values significantly. The moisture content of the panels was around 7%.

Table 1. Mechanical Properties of Both Particleboards

	MOE (MPa)	MOR (MPa)	IB (MPa)
Control boards	1,412	15.47	0.44
Chitosan treated boards	1,189	13.63	0.80

CONCLUSIONS

1. Physical properties of laboratory-made particleboard panels were improved with chitosan treatment. Thickness swelling, water gain, and linear expansion of panels decreased following high-heat treatment after application of chitosan, when compared with untreated control panels. Water-soluble chitosan acetate converted water-insoluble chitin during high-heat treatment. This chitin film acts as a water barrier layer around the chips, which significantly reduced the thickness swelling, linear expansion, and water gain of the chitosan treated panels.
2. The chitosan-treated board exhibited higher internal bond strength than untreated control panels. Bending strength and stiffness were negatively affected by high-heat applied chitosan treatment. In cases where mechanical properties are not so important, high-heat applied chitosan application on wood chips can be used in manufacturing of particleboards. Nonetheless, weak bending strength could be due to high heat effects on wood particles, rather than the chitosan treatment; this possibility should be considered in future research.

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