MOISTURE SORPTION PROPERTIES OF COMPOSITE BOARDS FROM ESTERIFIED ASPEN FIBER

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ABSTRACT

One barrier to producing wood-plastic composites with wood fiber is the poor thermoplasticity of wood fiber. The objective of our study was to determine the plasticization of chemically modified wood fiber through tests on unmodified and esterified fiberboards. Attrition-milled aspen fiber was esterified with neat acetic, maleic, or succinic anhydride. Fourier transform infrared spectroscopy, gas liquid chromatography, and titrational methods were used to confirm derivatization and to characterize the end products of the esterification reaction. All anhydrides formed a simple monoester; succinic anhydride was found to be the most reactive anhydride with a molar gain of 6.0 mol anhydride per kilogram wood fiber. Gains of 4.5 and 2.0 mol anhydride per kilogram wood were found for fiber modified with acetic anhydride and maleic anhydride, respectively. Scanning electron micrographs of hot-pressed fiber mats indicated that esterification of the aspen fibers with maleic or succinic anhydride imparted thermoplasticity to the fibers, whereas acetylation did not affect thermal properties. Fiber modified with succinic anhydride appeared to exhibit the greatest thermoplasticity. Esterified fiber in fiberboards made with phenol-formaldehyde as an adhesive or combined with polypropylene to form polymer-wood fiber composites had reduced moisture sorption and reduced rate of swelling in liquid water. Polypropylene also imparted temporary water repellency to the fibers.

Keywords: Esterification, acetic anhydride, aspen, composites.

INTRODUCTION

Previous investigators have demonstrated that moldable products can be produced by extensively modifying wood meal by chemical means or by incorporating wood flour as a filler

with thermoplastic polymers to produce thermoformable composites. However, these approaches do not fully exploit the beneficial features of the wood fiber. If wood fiber were used in place of wood flour, it may be possible to use the strength of the wood fiber to greatly improve the mechanical properties of the wood-plastic composites made by extrusion technology, injection molding, or film blowing. Two major problems need to be addressed before this type of technology can be fully exploited. One is to improve the thermoplasticity of wood fiber. The other is to improve the compatibility of the wood fiber with thermoplastics.

Chemical modification of wood has been used to improve the undesirable characteristics of wood such as dimensional instability, flammability, and biological, ultraviolet, and chemical degradation (Rowell 1983). Recent studies have focused on improving the thermoplasticity of wood through chemical modification. The hydroxyl groups of wood are most often the reactive sites. Researchers have investigated cyanoethylation (Hon and San Luis 1989), benzylation (Hon and Ou 1989), and reactions of trifluoroacetic (Shiraishi and Yoshioka 1986), and succinic anhydrides (Matsuda 1987) with wood hydroxyl groups.

The use of wood flour and other cellulosic fillers in wood-plastic composites was reviewed by Seymour (1978). Ideally, inexpensive, higher performance wood fiber and polymer composites could be produced in which any stresses applied to the composite would be transferred from the plastic polymer matrix to the stronger wood fiber if polymer matrix and wood fiber were fully compatible and good interfacial adhesion occurred.

We are currently taking two research approaches to developing moldable products from wood fiber: (1) plasticization and compatibilization of the wood through chemical modification, and (2) combination of the modified wood fiber with thermoplastics.

The aims of the research reported here were to (1) react wood fiber with different types of anhydrides, (2) determine the plasticization of

the reacted wood fiber, (3) make fiberboards with unmodified and esterified fiber using either a thermosetting or thermoplastic resin as binder, and (4) determine the moisture sorption properties of the fiberboards and the rate and extent of swelling in liquid water.

EXPERIMENTAL

Esterification procedure

Attrition-milled aspen fiber and solid southern yellow pine were acetylated using a simplified procedure developed by Rowell et al. (1986). The substrate was soaked in neat acetic anhydride (AA) for 15 min. The fiber was then allowed to drain and placed in a reactor at 120 C for different periods of time to give different levels of chemical weight gain. A vacuum was applied for 10 min to remove as much excess AA and byproduct acetic acid as possible. The esterified fiber was then oven-dried at 105 C for 3 days to further remove excess reagent and byproduct.

Aspen fibers were modified with maleic anhydride (MA) and succinic anhydride (SA) by the following procedure. Hot xylene was saturated with each anhydride in a reaction vessel. When reflux temperature was reached, the fiber was added and allowed to react for different periods of time to give different levels of chemical weight gain. Excess anhydride was removed by Soxhlet extraction of the esterified fiber with xylene for 4 h. Excess xylene was removed by evaporation and the fiber was then oven-dried for 3 days.

Analysis of esterification products

Fourier transform infrared (FTIR) spectroscopy was performed using a Nicolet 6000 spectrophotometer.[2] Samples of each modified product were dried, ground, and mixed with potassium bromide in a ratio of 1:200 mg and pressed under a vacuum to form pellets. Absorbance was measured from 4,000 to 400 cm^{-1}

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[2] The use of trade or firm names in this publication is for reader information and does not imply endorsement by the U.S. Department of Agriculture of any product or service.

TABLE 1. *Press conditions for production of aspen fiberboards with various amounts of polypropylene.*

Polypropylene (percent of total dry mat weight)	Press temperature (°C)	Press time (min)
0	210	5
2	210	5
10	190	5
25	175	10
50	170	15

with air as a reference. Scanning electron micrographs (SEM) were taken at 750× magnification with a Jeol 840 scanning electron microscope. All samples were coated with gold.

Acetyl contents were determined by saponifying the acetyl groups and measuring the liberated acetic acid using gas-liquid chromatography (GLC) with propionic acid as a standard. The ester content of the MA- and SA-modified fibers was calculated from the acid and saponification values using a technique similar to that used by Matsuda (1987). Titration of the free carboxyl groups in the esterified wood fiber and in ester groups saponified from the esterified wood fiber gave determinations of the ester content based on the acid and saponification values and indicated whether the anhydride added as a monoester or diester.

Fiberboard formation

Fiberboards were made with unmodified and modified (esterified) wood fiber and with no resin, a thermosetting resin, or a thermoplastic resin.

No resin.—Unmodified fibers and fibers modified with AA, MA, and SA were hand-formed into mats and pressed in a heated Carver press at 210 C for 5 min at 8.55 MPa (board pressure).

Thermosetting resin.—A liquid phenol-formaldehyde dry-process hardboard resin (GP 2341, diluted to 25% solids content) was sprayed onto the unmodified or esterified fiber. The fiber mat was manually formed by sprinkling fiber onto a screen to form a mat approximately 15 by 15 cm; the mat was then pressed in a heated Carver press at 190 C for

FIG. 1. Esterification reactions for aspen fiber reacted with (a) acetic anhydride or (b) maleic anhydride (when R is —HC=CH—) or succinic anhydride (when R is —CH₂—CH₂—).

10 min to a predetermined thickness of 0.6 cm and target board density of 0.7 g/cm³.

Thermoplastic resin.—A fibrillated form of polypropylene fiber from Hercules, Inc. (Pulpex, grade AD-H) was premixed by combining the polypropylene with the unmodified or esterified aspen fiber. The fiber mix was formed into a mat approximately 15 by 15 cm and pressed in a heated Carver press at 3.83 MPa (board pressure) for various times depending on the percentage of polypropylene. The resulting board densities varied from 1.15 to 0.85 g/cm³, decreasing as the polypropylene content increased. Press temperatures and times are given in Table 1. A minimum of five boards were made and tested.

Fiberboard testing

Moisture sorption.—Fiberboards were cut into 5- by 5-cm specimens and placed in separate rooms at 27 C and 30, 65, or 90% relative humidity. Each specimen was weighed at the end of 21 days and the equilibrium moisture content (EMC) determined. A minimum of five samples were tested and the results averaged.

Rate and extent of swelling.—Fiberboards cut into 5- by 5-cm specimens were soaked in water at room temperature, and changes in board thickness were measured at various intervals until the specimen reached a constant thickness. The intervals (from time zero) were as follows: 20, 40, and 60 min; 1, 2, 3, 4, and 5 h; and every 24 h. The percentage increase
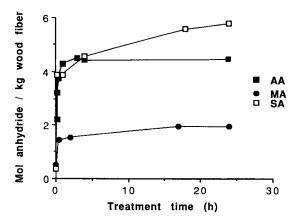
Fig. 2. Molar gains of aspen fiber esterified with acetic (AA), maleic (MA), and succinic (SA) anhydrides.

Fig. 3. FTIR spectra for control and esterified aspen fiber. AA is acetic anhydride, MA maleic anhydride, and SA succinic anhydride.

in thickness was calculated based on the original oven-dry thickness. A minimum of five samples was tested, and the results were averaged. The specimens were again oven-dried, and thickness and swelling were redetermined. The specimens were reimmersed in water and the thickness was measured after 1 week. The 7-day cycle was repeated until specimens no longer increased in thickness from cycle to cycle.

RESULTS AND DISCUSSION

Esterification of wood fiber

The esterification reactions of AA, MA, and SA with wood are shown in Fig. 1. Esterification of wood with AA resulted in the production of acetic acid as a byproduct; reactions with MA and SA resulted in the addition of 100% anhydride carbon skeleton to the wood.

Figure 2 shows the extent of modification achieved with the three types of anhydrides in terms of molar gain. The MA-modified wood showed much lower reactivity than the SA-modified wood, which had the same structure except for the double bond in MA. This was probably due to the higher activation energy for reaction of MA compared to SA.

Figure 3 compares FTIR spectra for the unreacted wood fiber (control) and various esterified wood fibers. The peak at approximately 1,720 to 1,750 cm^{-1} represents the C=O
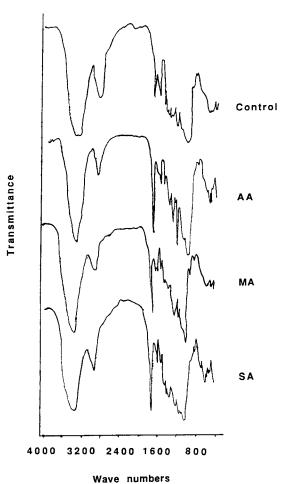
of the esterified wood fiber and shows that the anhydrides reacted with hydroxyl groups in the cell wall. The split peak at 1,640 cm^{-1} in the FTIR spectrum of the MA-modified wood fiber shows that the double bond remained intact.

Equivalent wave numbers were obtained when the ester content was calculated based on the acid and saponification values, indicating that the anhydride was added as a monoester and not as a diester for each reaction system—that is, the ester content based on the number of free carboxyl groups and the total number of carboxyl groups present after
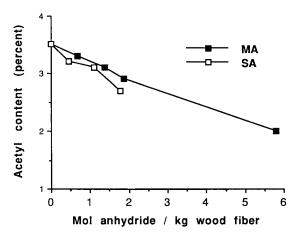
FIG. 4. Transesterification of hemicellulosic acetyl groups by maleic (MA) and succinic (SA) anhydrides.

anhydride modification indicated that the anhydride was added as a monoester. The ester content based on the acid and saponification values also agreed with the calculated percent weight gain for each reaction system.

Because the acetylation reaction cannot result in free carboxyl formation, there was no need to check for diester formation. The acetyl content of the acetylated fiber as analyzed by GLC agreed with the calculated percent weight gain.

Figure 4 shows the decrease in the natural acetyl content of the wood fiber during MA and SA esterification reactions, which resulted from transesterification. Because the acetyl groups are found only in the hemicelluloses of the wood, transesterification demonstrates that hemicelluloses were involved in the esterification reaction. No decrease in the acetyl content was found when the aspen fiber was refluxed in xylene for 24 h. The loss of acetyl groups was apparently caused not by the high reaction temperatures but rather by the transesterification reaction.

Esterification of solid wood

To obtain further evidence of anhydride bonding in the cell wall, solid blocks of southern yellow pine were reacted with each anhydride. The molar gains of the solid wood were almost the same as the molar gains of the wood

fibers except that MA reacted to a lesser extent in the solid wood as compared to the fiber. A molar gain of 0.5 mol anhydride per kilogram was obtained for MA in solid wood compared to 2 mol anhydride per kilogram for wood fiber.

The actual volume increase in solid wood resulting from esterification was measured after reaction. At <30% weight gains, the volume increase (from original oven-dry volume to re-oven-dried esterified volume) resulting from bulking of the cell wall was proportional to the amount of anhydride added. For the SA-modified pine blocks with >30% weight gains, the volume increase was larger than expected. The SEM displayed severe splitting of the cell walls of the blocks (Fig. 5), which explains the unusually large volume increase. The phenomenon of cell-wall rupture caused by high chemical reaction weight gains was reported by Rowell and Ellis (1981). When the volume of chemical added to the cell wall exceeds the original volume of water in the green cell wall, the cell wall splits to accommodate the additional chemical.

Moisture sorption of esterified fiber and fiberboards

Figure 6 shows that the EMC of the esterified fiber was independent of the type of esterification but dependent on the molar gain of reacted ester in the wood fiber. For each type of anhydride, EMC decreased as the level of modification increased.

As with the esterified wood fiber, the EMC of fiberboards made with phenol-formaldehyde resin was not influenced by the type of esterification but was significantly affected by the level of modification. A proportional reduction in EMC occurred as the level of modification increased for each type of esterification; a 25% reduction in EMC was obtained at a molar gain of 3 mol anhydride per kilogram.

Figure 7 shows the EMC for unmodified and acetylated aspen fiber in combination with polypropylene fiber. As the amount of polypropylene increased, the EMC decreased. This
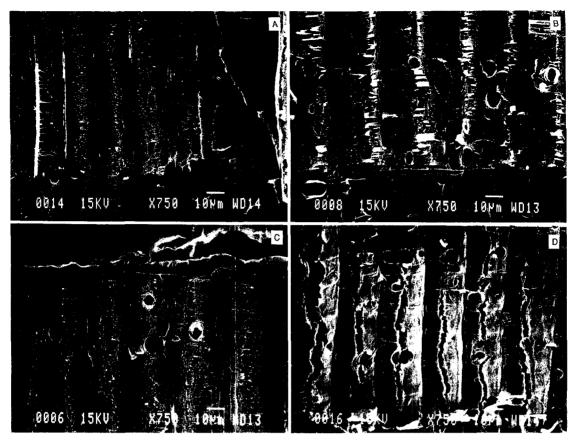
FIG. 5. Scanning electron micrographs of southern yellow pine blocks. A, Control. B–D, Blocks modified with different anhydrides (weight percent gain in parentheses): B, acetic (22%); C, maleic (4.5%); and D, succinic (61%).

was probably due to the coating effect of polypropylene on the wood fiber after hot pressing. The wood fiber had become water repellent as a result of the polypropylene coating, especially at high polypropylene levels (>50%).

Rate and extent of fiberboard swelling in liquid water

Increase in thickness of fiberboards bonded with phenol-formaldehyde resin showed the same trends as those of the EMC of the humidified fiber boards. Thickness increase was independent of the type of esterification but dependent on the level of esterification. A 25% reduction in thickness swelling was achieved at a level of modification of 3 mol anhydride per kilogram of dry fiber.
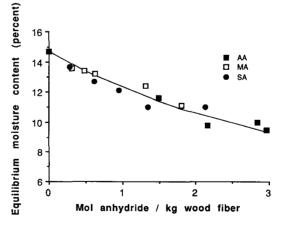

FIG. 6. Equilibrium moisture content of aspen fiber esterified by reaction with acetic (AA), maleic (MA), and succinic (SA) anhydrides.
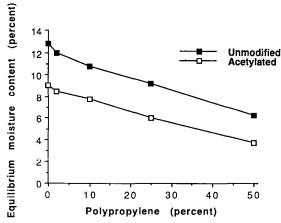
FIG. 7. Equilibrium moisture content of unmodified or acetylated aspen fiber compared to polypropylene content.
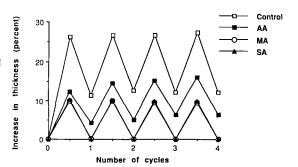

FIG. 9. Increase in thickness during cyclic water-swelling tests of control fiberboards and fiberboards modified with acetic (AA), maleic (MA), and succinic (SA) anhydrides and 5% phenol-formaldehyde resin.

Figure 8 shows the rate of polypropylene-bonded fiberboard swelling in liquid water. Although control boards swelled almost 25% in thickness in the first 20 min, all types of esterified boards swelled less than 10%. Acetic anhydride reduced swelling to less than half the swelling of the control specimens, whereas MA and SA reduced swelling even further. The reduction in swelling can be attributed to the bulking of the cell wall and the reduction of the capillary action of the wood, especially with the larger MA and SA molecules. A possible increase in thermoplasticity and subsequent

increase in bond strength caused by increased fiber-to-fiber contact during hot pressing could also help explain the reduction in swelling.

The results of cyclic wetting and drying tests on phenol-formaldehyde-bonded fiberboards are shown in Fig. 9. Reversible swelling (normal swelling and shrinking of the fiber cell wall) was reduced by all types of esterification. Fiberboards modified with AA showed reversible swelling of about 8% compared to the 15% reversible swelling of control boards. Reversible swelling of MA- and SA-modified boards was about 10%. The major effect of the type of anhydride used for modification was shown in irreversible swelling (permanent increase in oven-dry thickness over several cy-
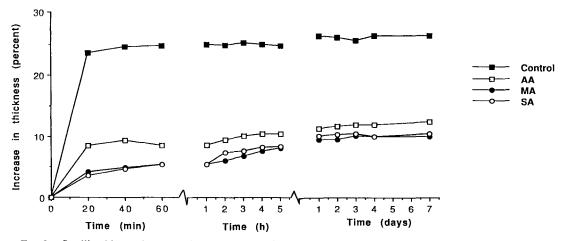

FIG. 8. Swelling history (water-soaked specimens) of control fiberboards and fiberboards modified with acetic (AA), maleic (MA), or succinic (SA) anhydrides and 5% phenol-formaldehyde resin.
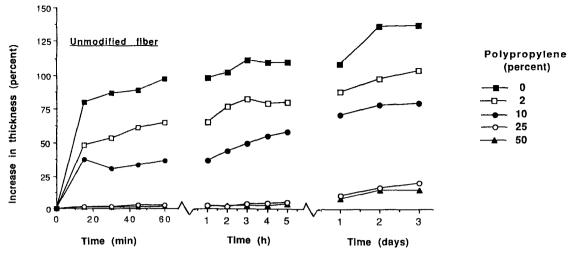
FIG. 10. Swelling history (water-soaked specimens) of fiberboards made with unmodified aspen fiber and various amounts of polypropylene.

cles caused by relief of the stresses induced during pressing of the board). Acetylated fiberboards had less than half the irreversible swelling of the unmodified boards. The MA- and SA-modified boards showed a complete absence of irreversible swelling as a result of an increase in thermoplasticity of the esterified fiber, which prevented the development of stresses during pressing. These results suggest that the SA- and MA-modified fibers underwent plastic deformation during pressing—the acetylated fiber recovered a portion of the induced deformation and the unmodified fiber recovered most or all the deformation. Relatively low molar gains of SA or MA (approximately 2 mol anhydride per kilogram wood fiber) resulted in a complete absence of irreversible swelling.
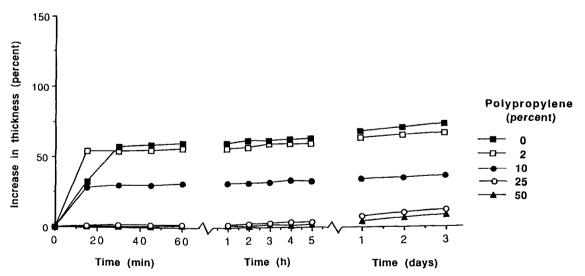

FIG. 11. Swelling history (water-soaked specimens) of fiberboards made with acetylated aspen fiber and various amounts of polypropylene.
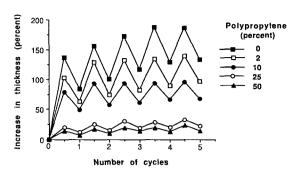
FIG. 12. Increase in thickness during cyclic water-swelling test of fiberboards made with unmodified aspen fiber and various amounts of polypropylene.

FIG. 13. Increase in thickness during cyclic water-swelling test of fiberboards made with acetylated aspen fiber and various amounts of polypropylene.

Figure 10 shows the rate and extent of swelling in liquid water of fiberboards made with unmodified aspen fiber and polypropylene. As the amount of polypropylene increased, both the rate and extent of thickness swelling decreased. Because the polypropylene only coated the unmodified fiber, providing water repellency, water could penetrate the unmodified fiber and cause it to swell in time. This is clearly seen in the curves for 25 and 50% polypropylene (Fig. 10). Very little swelling occurred in these bonds in the first 5 h; swelling began after 24 h and continued to increase during the following 3 days.

Figure 11 shows the rate and extent of swelling in fiberboards made with AA-modified fibers and polypropylene. Less swelling occurred in all boards as compared to unmodified boards, and swelling did not increase very much after the first 30 min of immersion. This shows the effectiveness of combining a cell-wall-bulking treatment (dimensional stability) with a cell-coating treatment (water repellency). Figure 11 also shows some loss of water repellency after 24 h of immersion.

Figures 12 and 13 show the cyclic water-swelling results for unmodified and acetylated fiberboards made with polypropylene. Much greater swelling occurred in these boards as compared to boards made with phenol-formaldehyde resin (Fig. 9). This may be due to the higher density of the boards with polypropylene compared to that of the phenol-formaldehyde-bonded boards, which could result in
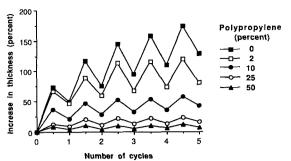
higher swelling. Better fiber-to-fiber bonding took place in the phenol-formaldehyde-bonded boards, which resulted in lower swelling. The effect of an increase in polypropylene content on cyclic water swelling was more pronounced than the effect of esterification. Both reversible and irreversible swelling were greatly reduced as the polypropylene content was increased to 50%. Maximum thickness swelling was about 15% in boards made with acetylated fiber and bonded with phenol-formaldehyde (Fig. 9) but about 50% in boards made with the same fiber plus 10% polypropylene (Fig. 13). These results indicate that polypropylene is not very effective as a fiber adhesive.

Plasticization of esterified fibers

Figure 14 shows SEMs of the faces of high density fiberboards made from unmodified and esterified fiber with no resin. All boards were pressed under identical conditions. The SEM of the AA-modified fiberboard (B) is quite similar to that of the unmodified fiberboard (A). The SEM of the MA-modified fiberboard (C) shows a more compact structure than A or B, possibly indicating an increase in thermoplasticity. The SEM of the SA-modified fiberboard (D) shows that the fibers became flattened and spread out, which indicates that some amount of thermoplasticity was achieved.

CONCLUSIONS

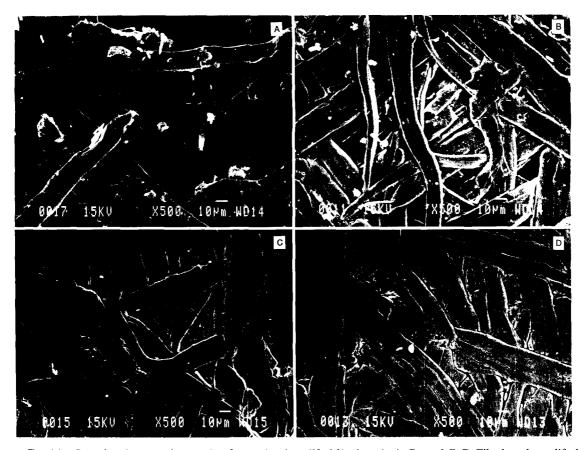Esterification with acetic, maleic, or succinic anhydride reduced equilibrium moisture con-

FIG. 14.   Scanning electron micrographs of control and modified fiberboards. A, Control. B–D, Fiberboards modified with different anhydrides (weight percent gain in parentheses); B, acetic (20%); C, maleic (20%); and D, succinic (58%).

tent in aspen fiber regardless of the anhydride used. Fiberboards made from esterified fiber showed greatly reduced reversible and irreversible thickness swelling. Irreversible swelling was completely eliminated in the case of fiber esterified with maleic or succinic anhydride. The blending of unmodified or esterified fiber with polypropylene and hot pressing produced boards with reduced equilibrium moisture content and reduced rates of water swelling. Polypropylene imparted water repellency to the fibers. However, this effect was not permanent, and water repellency was greatly reduced after extended water soaking.

Esterification with either maleic or succinic anhydride resulted in thermoplasticization of the wood fiber. Research is continuing on plasticization of wood fiber and the compatibility of wood fiber with plastic materials.

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