BIOLOGICAL RESISTANCE OF POLYETHYLENE COMPOSITES MADE WITH CHEMICALLY MODIFIED FIBER OR FLOUR

Rebecca E. lbach and Craig M. Clemons

USDA Forest Service, Forest Products Laboratory*
One Gifford Pinchot Drive
Madison, WI 53726 USA
ribach@fs.fed.us

Keywords: composites, polyethylene, chemical modification, acetic anhydride, butylene oxide, propylene oxide, equilibrium moisture content, decay, mechanical properties

ABSTRACT

The role of moisture in the biological decay of wood-plastic composites was investigated. Southern pine wood fiber and ponderosa pine wood flour were chemically modified using either acetic anhydride (AA), butylene oxide (BO), or propylene oxide (PO). A 50:50 mixture of high-density polyethylene and either chemically modified fiber or flour, or untreated fiber or flour was compounded (blended) and then compression molded. After preconditioning specimens either by a 2-week water soaking or a 5-day boil/dry cycling, a modified soil block test with the brown-rot fungus Gloeophyllum trabeum was performed. Weight loss, moisture content, and mechanical properties were measured after 12 weeks of fungal exposure. The equilibrium moisture content at 30%, 65%, and 90% relative humidity and 27 °C was determined.

Results show a correlation between moisture and decay. Weight loss from decay increased with increasing specimen moisture content (MC). Ranking of the specimens from the lowest weight loss and MC to the highest are as follows: AA<BO<Control<PO. This indicates the mechanism of efficacy of chemically modified wood-plastic composites may be by lowering the cell wall moisture content below the level required for microorganism attack.

INTRODUCTION

Wood is a polymeric composite consisting mainly of cellulose, hemicelluloses and lignin that contain accessible hydroxyl groups and other oxygen containing groups that attract moisture through hydrogen bonding making wood hygroscopic (Stamm 1964; Rowell and Banks 1985). Chemically reacting these hydroxyl groups of wood with various chemicals can make the wood more hydrophobic by eliminating sites for hydrogen bonding of water (Rowel1 1983; Kumar 1994; Militz *et al* 1997). Fungi need water to breakdown wood. Literature states the moisture content (MC) of wood needs to be above the saturation point (25-30% MC) for decay to occur (Carll and Highley 1999). By chemically modifying wood it can still be exposed to water or wet conditions, but it will sorb little cell wall water.

Investigating the relationship between MC and decay by chemically altering the structure of wood is ongoing. Three different chemicals were chosen for modifying solid wood and fiber: acetic anhydride (AA), butylene oxide (BO), and propylene oxide (PO). Previous research has shown a decrease in the equilibrium moisture content (EMC) and an increase in fungal resistance

* The Forest Products Laboratory is maintained in cooperation with the University of Wisconsin. This article was written and prepared by U.S. Government employees on official time and is therefore in the public domain and not subject to copyright. 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.

after southern pine solid wood and fiber was chemically modified by AA or BO, indicating a mechanism of efficacy by lowering the moisture content of wood below the level required for microorganism attack (Ibach *et al* 2000). Yet, the fiber modified by PO did not lower the EMC, but did provide some fungal resistance in soil block testing which suggested a substrate modification mechanism, thus rendering the wood as a non-food source.

The wood-plastic composites (WPC) industry is growing rapidly in the United States in many building applications such as decking, fencing, flooring, landscape timbers, railings, moldings, roof shingles, siding, and waterfront applications (Clemons 2002). It is thought that when using plastic and wood together, the wood is encapsulated in the plastic, therefore improving its moisture resistance and durability, (depending on % wood content) but there is little scientific literature to support this assumption. Because of the biological effectiveness and moisture resistance of the chemically modified fiber, this research was undertaken to assist in addressing the role of moisture in the decay of WPC's.

This paper deals with the fungal durability of compression molded WPC's (50% wood, 50% plastic) with respect to moisture sorption. The objectives were to chemically modify not only wood fiber, but also wood flour (which is commonly used in the industry); compression mold with high density polyethylene (HDPE); determine the fungal resistance, moisture content, EMC, and mechanical properties; and determine if there is a correlation between weight loss, moisture content and mechanical properties.

MATERIALS AND METHODS

The wood filler was either western pine wood flour, with a nominal 40 mesh (420 µm) from American Wood Fiber (Schofield, WI), or southern pine fiber from Templen Forest Products Corporation (Lubbock, TX). The flour and fiber were modified with three different chemicals: 1 .) acetic anhydride, 2.) butylene oxide, or 3.) propylene oxide. Acetic anhydride and butylene oxide were from Eastman Chemical Company (Kingsport, TN), and propylene oxide and triethylamine (the catalyst) were from Aldrich Chemical Company (Milwaukee, WI).

The plastic material was HDPE from reprocessed milk bottles (Muehlstein and Co., Inc., Roswell, GA), with a melt flow index of approximately 0.7 g per 10 min.

Chemical Modifications of Wood Fiber and Flour

Southern pine fiber was screened and washed to remove fines, and then oven dried before chemical modifications. The western pine flour was only oven dried before treatment.

Acetic Anhydride: The fiber or flour was boiled in acetic anhydride in a one-liter glass reactor for 4 hours. The treated fiber or flour was washed, oven dried, and weight gain percentage (WPG) calculated. Percentage acetyl content was determined on acetylated fiber and flour, as well as untreated controls using anion exchange high perfomance liquid chromatography (HPLC) with a suppressed conductivity detector. Previously described method was followed (Ibach et al 2000).

Butylene Oxide and Propylene Oxide: Oven dried fiber and flour were weighed and then reacted in a stainless steel reactor with a mixture of propylene oxide or butylene oxide and triethylamine (955 (vol.:vol.)) at 120 °C and 150 psi nitrogen pressure, for 4 hours for butylene oxide and I hour for propylene oxide (Rowell and Gutzmer 1975). The treating solution was drained off. Samples were air dried under a fume hood, oven dried, and WPG calculated.

Compression Molding

Wood flour or fiber was compounded with HDPE in a 1-liter high intensity thermokinetic mixer (K Mixer, Synergistics, Inc., St. Remi de Napierville, Quebec). The thermokinetic mixer is a simple batch mixer in which several high-speed blades supply the energy to melt the polymer and blend the material. An infrared sensor monitors the material temperature. Batches of 60 g each of HDPE and wood flour were processed at 5,500 rpm (rotor tip speed of about 30 m/s) with a discharge temperature of 170 °C and a batch time of about 150 s. After discharging, the blended material was hot pressed to 3 mm thickness at 180 °C for 1 minute and then cooled in the press until solidified. Board thickness was achieved by pressing to a metal ring 3-mm thick with sufficient inner diameter to accommodate the batch volume. Teflon-coated cauls were used to aid in separating the boards from the cauls after pressing. Specimens (13 by 89 mm) were cut from the pressed boards.

Specimen Conditioning

Specimens were exposed to one of two conditioning procedures to accelerate moisture sorption: 1.) 14 day water leaching (AWPA 1999), or 2.) 5 cycles of a 2-hour boil followed by 24 hours of oven drying. After preconditioning, oven dried specimens were placed in a 65% relative humidity and 27 °C room for 4 weeks before fungal decay testing.

Biological Evaluation

To evaluate fungal resistance a modified ASTM D1413 soil block test was performed (ASTM 1999). Modifications include 1 .) changing the specimen size from 19 by 19 by 19 mm to 3 by 13 by 89 mm, 2.) turning the standard soil bottle on its side to accommodate the 89 mm length, 3.) using a longer feeder strip and several fungal inoculations along the specimen length, 4.) adding flexural tests to correlate strength loss with weight loss, and 5.) measuring the moisture content of the specimens before and after fungal inoculation. Specimens were exposed to the brown-rot fungus, *Gloeophyllum trabeum* (Madison 617) for 12 weeks. Five specimens were tested, averaged, and standard deviations calculated.

Equilibrium Moisture Content

The EMC of all specimens was determined consecutively in 3 different conditioning rooms: 30%, 65%, then 90% relative humidity (RH); all at 27 °C. Specimens were oven dried at 105 °C for 24 hours and weighed. The EMC was determined after 6 weeks at 30% RH, 16 weeks at 65% RH, and 13 weeks at 90% RH. Specimens were weighed weekly. Six specimens were tested, averaged, and standard deviations calculated. These specimens were not used for decay testing.

Mechanical Testing

Four-point flexural tests were performed on oven-dried specimens according to ASTM D 790-84 (ASTM 1990). Maximum stress, initial tangent modulus, and the work required to reach maximum load were determined before and after 12 weeks fungal exposure. In all cases, failure occurred between the load points in the center third of the specimen. Five specimens were tested, averaged, and standard deviations calculated.

RESULTS AND DISCUSSION

Chemical Modifications

The WPG's from chemical modification with AA, BO, and PO fiber and flour are presented in Table 1. Because of the lower than expected WPG after 4 hours of modification with the acetylated fiber, the acetyl content was determined on the controls, as well as the acetylated fiber and flour. The percentage acetyl content (20.1% acetyl) was much higher for the acetylated fiber than just weight gain (12.6 WPG), and only slightly higher for the flour (22.9% acetyl and 20.1 WPG). The fiber was screened, washed, and dried before acetylation to remove the fines, but there was still a significant loss of fiber during the acetylation procedure to accurately determine WPG. Hence, the percentage acetyl is the more accurate measurement. With this in mind the BO and PO WPG's, especially for fiber, may also be higher but to date we have no analytical method developed. The reaction times were based on previous research (Ibach *et al* 2000).

Specimen Conditioning

To precondition the specimens before decay testing, either a 14-day water soaking or a 5-day boil/dry cycling was performed to accelerate the moisture sorption. The standard water leaching procedure is used before soil block testing in solid wood to test the extent of chemical weight loss. There was no significant weight losses of the WPC's after 2 weeks water leaching. The 5 cycles of a 2-hour boil followed by 24 hours of oven drying simulated the wet-dry cycling that occurs naturally in outdoor exposures.

Biological Evaluation

Figure 1 shows the moisture absorbed by the chemically modified WPC's after the 12-week soil block test with the brown-rot fungus *G. trabeum.* For the unmodified control specimens, the water soaking gave slightly lower moisture contents than the boiled. This is due to interfacial damage caused by each boil/dry cycling, thereby allowing more moisture sorption for each successive cycle (Clemons and Ibach 2002). The chemically modified specimens did not show the same trend. Perhaps this is because the wood component did not shrink and swell due to the hydrophobic nature of the wood after chemical modification. This would mean less interfacial damage.

The moisture sorption after fungal decay was lowest for the AA, followed by the BO and then the PO modified specimens. To prevent fungal decay in solid wood the MC needs to be below the fiber saturation point (about 25% to 30%). HDPE absorbs no moisture, so the wood MC's should be about twice that shown in Figure 1. Hence, keeping the MC of the composite below 12.5% (25% wood MC) should prevent fungal attack, which seems to be the case.

Figure 2 shows the weight losses of the composites after fungal exposure in the 12-week soil block test. Overall the weight losses were low (<4% composite weight loss or <8% weight loss of the wood content). For solid wood <5% weight loss is considered a success in the soil block test. With this criteria, the controls and the PO modified composites would be considered a failure, the BO would have moderate success, and the AA modified specimens would be a success. The BO boiled specimens have large standard deviations compared with the water soaked specimens. Overall, the boiled specimens have higher weight losses than the water soaked specimens, Again this could be due to creating small pathways in the composite from the harsh boil/dry preconditioning (especially the surface) to allow accessibility of the fungi.

Figure 3 shows the correlation between the fungal weight losses and the MC after 12 weeks of fungal exposure. Even with the low weight losses, the 12.5% total composite MC (25% wood MC) rule seems to apply. This same correlation has been found with WPC made by extrusion and injection molding (Clemons and Ibach 2002). The AA and BO specimens are below 12.5% composite MC or 25% wood MC, and the PO and unmodified controls are above the 25% wood MC.

Equilibrium Moisture Content

Figure 4 shows the EMC of the composites exposed to 30%, 65%, and 90% RH, and 27 °C. With increasing relative humidity (constant temperature) the differences between the composites is enhanced. Similar to the percentage moisture content of the specimens removed after the decay test, the EMC is highest for the control and PO, followed by the BO and then the AA modified specimens. For the control, PO, and BO modifications, the specimens made with wood fiber have higher overall EMC values than the specimens made with wood flour.

The rate of moisture sorption in the 90% RH conditioning room is presented in Figure 5. Over 63 days of conditioning the composites made with fiber have come to equilibrium, but the composites made with flour continue to increase in moisture uptake. This research continues to be monitored.

Mechanical Testing

Loss in the mechanical properties of wood has been used as a measure of incipient fungal decay (Wilcox 1978; Winandy and Rowell 1984). The purpose of the wood flour in WPC's is as filler and thus does not contribute greatly to the strength of the composite. Therefore the effect on the strength of the WPC from fungal decay is not expected to be as great as that of solid wood. However, it was thought that determining the mechanical property loss may help corroborate the weight loss results.

Figure 6 shows the effect on the flexural modulus of the water soak and the boil preconditioning of unmodified fiber controls as well as the modified composites. The initial specimens had no preconditioning. The control shows a lowering of the flexural modulus due to the water soak and boil preconditioning. This negative effect of moisture sorption on the mechanical performance of WPC's makes it difficult to assess the loss due to just moisture or decay during the soil block test. There is a decrease in flexural modulus of the PO, BO, and AA initial specimens. The preconditioning of the BO and PO composites shows some decrease of the modulus, but there is little effect with the AA composites.

Figure 7 shows the loss in stiffness of the fiber composites during the soil block test. There seems to be an effect on the modulus loss between the AA composites and the controls, but the standard deviations are so high that they are not significant. Mechanical property loss appears less sensitive than weight loss, especially for early detection of fungal decay of WPC's.

In recent work a correlation between strength loss versus weight loss, as well as modulus loss versus weight loss was found with both injection molded and extruded composites (Clemons and Ibach 2002). However, compression molded specimens did not follow the trend. Research continues in this area.

SUMMARY AND CONCLUSIONS

Chemical modification of wood fiber and flour for use in WPC's was performed to study the role of moisture in the decay mechanism of compression molded composites. Preconditioning before fungal exposure was used as a means to accelerate the moisture sorption in the soil block test. Mechanical testing before and after chemical modification and fungal

exposure was performed to assess any correlation between strength loss and weight loss. Due to high standard deviations, mechanical testing was found to be less sensitive than weight loss in assessing biological decay of compression molded composites.

Overall the composites had low weight losses in the soil block test, but this is consistent with the slower moisture sorption due to the plastic matrix. The unmodified controls and PO composites had the highest moisture contents and weight losses after decay, and PO did not lower the EMC. These results are consistent with previous work with PO modified solid wood (Ibach *et al* 2000). The BO modification slightly lowered the EMC and the moisture content after decay, and resulted in moderate biological efficacy compared to the controls. Modification with AA resulted in lower moisture content and no weight loss after decay; lower EMC values; and little effect on the flexural modulus due to preconditioning by water soaking or boiling. Laboratory research continues on the role of moisture in biological deterioration, as well as field testing, which involves other degradation mechanisms such as UV light and freeze-thaw temperatures.

ACKNOWLEDGEMENTS

Our sincere thanks to Beom-Goo Lee, Rebecca Schumann, Sandy Lange, and Brian Destree from the Forest Products Laboratory for their assisstance with this research. The authors also acknowledge Mark Davis from the Forest Products Laboratory for performing acetyl analysis.

Table 1. Weight percentage gain (WPG) and percentage acetyl content of southern pine wood fiber and western pine wood flour after chemical modification with acetic anhydride (AA), butylene oxide (BO), or propylene oxide (PO).

	Chemical Modification	WPG (%)	Acetyl (%)
Fiber	None	0.0	1.14 (0.01)
	AA	12.6	20.05 (0.36)
	BO	16.1	
	PO	23.4	
Flour	None	0.0	1.87 (0.02)
	AA	20.1	22.94 (0.15)
	BO	22.0	
	PO	30.8	

Proceedings

The 6th Pacific Rim Bio-Based Composites Symposium

&

Workshop on

The Chemical Modification of Cellulosics

Portland, Oregon, USA

2002

VOLUME 2

PROCEEDINGS OF

THE 6TH PACIFIC RIM BIO-BASED COMPOSITES SYMPOSIUM

&

WORKSHOP ON
THE CHEMICAL MODIFICATION OF CELLULOSICS

PORTLAND, OREGON, USA

2002

VOLUME 2

Compiled by
Philip E. Humphrey

Symposium Organisers

Department of Wood Science and Engineering, Oregon State University, Corvallis, Oregon 97331, USA

Symposium Sponsors

Oregon State University, College of Forestry
U.S. Borax
Dynea USA
Adhesive Evaluation Systems Inc.
Steven Young and Associates
DoubleTree Hotel, Lloyd Center

Publisher

Published by the Wood Science and Engineering Department, Oregon State University, Corvallis, Oregon, 97331, USA.

Publication date: October 27*. 2002.

Copyright Notice

Disclaimer of Liability for Information