

Bio-Based Adhesives and Reproducible Rapid Small-Scale Bond Strength Testing

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Abstract

Soy flour is an inexpensive raw material for adhesives and is readily available in most parts of the world. However, converting soy flour into a wood adhesive that can compete in both cost and performance with existing petroleum-based adhesives is not easy given the variables of flour quality, denaturation conditions, and curing methods. Formulating adhesives that alter these variables is more readily accomplished than is testing the performance of these formulations using standard evaluation methods. To overcome this problem, we developed a rapid and reproducible small-scale bond strength testing procedure that allows us to screen new adhesives more efficiently. This procedure, employing the automated bond evaluation system (ABES) instrument, has led to improved soy adhesive formulations for plywood and other wood-bonding applications. Additionally, this procedure has been compared with standard product performance tests for decorative and exterior plywood using the common commercially available adhesives poly(vinyl acetate), urea-formaldehyde, melamine-urea-formaldehyde, and phenol-formaldehyde.

Introduction

The increased price of petroleum and environmental concerns about some current wood adhesives have led to an increased interest in bio-based adhesives. Although bio-based adhesives have been used for thousands of years, they play only a very minor role in current wood-bonding markets. Of the bio-based feeds, soybeans are of interest because of their large production volume and relatively low cost.

Research on soybean utilization for chemical products has been extensive, but much of it has been on the oil portion rather than the remaining meal after oil extraction. In the past, this meal was ground into flour and used as one of the first adhesives for interior plywood. However, traditional soy flour products do not have good enough water resistance to meet today's higher performance standards. The large rise in petroleum prices in the past decade and relatively stable prices for agricultural crops have led to a favorable market for bio-based adhesives, assuming that their performance can compete with that of current products.

Some recent research has focused on developing adhesives from soy flour (Hse et al., 2001; Wescott et al, 2006), but even more research has been done using protein isolates that are derived from soy flour (Li et al., 2004; Sun, 2005; Zhong et al, 2007). Given the higher cost and limited availability of soy protein isolates, we have focused on the development of durable (water-resistant) adhesives from low-cost soy flour.

In developing these new soy-based adhesives, the time-consuming sample preparation and testing of adhesive performance often slows the development process. Although several adhesive formulations can be made in a day, each resin can take several days to test using conventional methodologies. Thus, we have examined ways to more rapidly screen the adhesives. In one such application, we were developing adhesives for the decorative plywood market. An important performance test for this application is the ability of the adhesive to hold the plywood together during a cyclical soak and dry test that takes three days to complete and provides only pass–fail data on each adhesive, with no actual quantification of the strengths (ANSI/HPVA HP-1-2004 4.6) (American National Standards Institute, 2004).

In our initial studies on soy adhesives, we successfully used an automated bond evaluation system (ABES) unit for testing adhesive cure rates. The ABES unit was developed to help understand strength development of an adhesive under various bonding conditions (Humphrey, 2006). We needed to design a test method that could take advantage of the rapid sample preparation feature of the ABES unit for forming a reproducible bond. We could then use a standard mechanical tester for examining bond strength before and after water soaking in order to screen out less promising adhesives. Moreover, we could better quantify changes to the formulation prior to performing the more time-consuming cyclical soak-dry tests. Given the success of this method with soy adhesives, we examined if this test was useful for other adhesives in both decorative or interior plywood tests and exterior plywood strength tests.

Experimental

Wood veneer sheets of 0.8-mm-thick maple (sugar maple, *Acer saccharinum*) and pine (eastern white pine, *Pinus strobus*) were supplied by States Industries (Eugene, Oregon) and stored at 22°C and 50% relative humidity. The sheets were cut into the specimen size of 20 by 117 mm using the ABES die cutter from Adhesive Evaluation Systems, Inc. (Corvallis, Oregon). The soy adhesives were made as described in a U.S. patent application (Wescott and Birkeland, U.S. Patent Application 60/831,650). The poly(vinyl acetate) (PVAc), urea-formaldehyde (UF), and melamine-urea-formaldehyde (MUF) were commercial products. The phenol-formaldehyde (PF) was made by reacting formaldehyde with phenol in a molar ratio of 2.08 under standard conditions. Wheat flour and wood flour fillers were used with the PF and UF resins.

The ABES was a standard unit from Adhesive Evaluation Systems, Inc. For the soy formulations, 0.038–0.042 mg/mm² of adhesive solution was applied to one surface on a 10- by 20-mm area. The coated and uncoated strips were bonded in the ABES using 0.25 MPa of pressure with the platens heated to 120°C. After 2.0 min, the pressure was released

and the sample was removed from the grips and allowed to cure and equilibrate at 22°C and 50% relative humidity. For the comparative testing program, the adhesive was applied and bonded at 120°C, except in the case of the PF resin, which was bonded at 150°C.

The ABES-bonded samples were tested for strength either at ambient conditions or after a 4-h water-soak on an Instron Model 1000 tensile strength tester (Norwood, Massachusetts) using a crosshead speed of 10 mm/min. After fracture of the sample, it was noted whether the adhesive or wood failed.

Using the PVAc, PF, MUF, and PF adhesives, we also compared results from standard test protocols with our results obtained on the small specimen test. For interior or decorative plywood, the standard test is ANSI/HPVA HP-1-2004 4.6 (hereafter referred to as HP-1) (American National Standards Institute, 2004). For exterior plywood, the standard test is the Voluntary Product Standard PS 1-95 6.1.5.1 and .2 (hereafter referred to as PS 1-95) (APA-The Engineered Wood Association, 1995). For these tests, veneers of the same wood species but 3.2 mm thick were used, with pieces 356 by 140 mm for PS 1-95 and 216 by 216 mm for HP-1.

Results and Discussion

Sun and other researchers have done considerable evaluation of ways to improve the bond strength of soy protein isolates (Sun, 2005). Our efforts have focused on using the more economical soy flour (Wescott et al., 2006; Wescott et al, 2006). Although the proteins are considered to be the main adhesive component of the flour, the flour often behaves differently because of the presence of lower molecular weight proteins and soluble and insoluble carbohydrates. In the past, we focused on caustic denaturation of proteins in the flour. However, other means can also be used to denature the flour. One way is to use urea and heat to denature the proteins, and this technology has been discussed in a recent patent application (Wescott and Birkeland, U.S. Patent Application 60/831,650).

For making commercially viable soy flour adhesives, one key issue is a balanced denaturation that (a) exposes more functional side groups of the globular proteins for increased adhesion to the wood but (b) retains enough secondary and tertiary structure for adhesive strength. Another key issue is to make bonds using water-borne soy flour adhesive more water resistant after the bonding process. Consequently, we wanted to test the strength of the bonded specimens not only in the dry state but also as wet assemblies after water soaking.

Our initial program was aimed at developing soy flour-based wood adhesives as face resins for strandboard (Wescott et al., 2006; Wescott et al, 2006), but we also wanted to develop adhesives for interior or decorative plywood. For this application, we needed to change our adhesive development strategy and our adhesive evaluation methods. The standard test method for interior or decorative plywood, HP-1, requires 10-15 work hours, ~72 h total time, and ~50-100 g of adhesive for each formulation and provides only a qualitative pass-fail result. To speed up the program, a more efficient way to screen the formulations was needed so that only the best performing resins were tested using the more

time-consuming standardized test. In addition, this new test should provide numeric values for evaluating changes in formulation rather than just a pass-fail evaluation.

The ABES unit had been successfully used in our soy formulation program to determine strength development with time at a given temperature, for which the ABES was originally designed (Humphrey, 2006). However, the ABES is also an effective unit for rapidly making small bonded samples under very controlled bonding pressures, temperatures, and times for use in other testing methods. In particular, we wondered if the ABES-bonded samples could be used to test water resistance of wood bonds for predicting the ability of an adhesive to pass the standard water-resistance test HP-1. Thus, in developing these new soy adhesives, we evaluated soy flour adhesives in both the standard test and our new ABES-tensile test. After ABES bonding, samples were removed from the unit to allow the adhesive to complete its cure and to adjust to its equilibrium moisture content. A suitable adhesive needs to provide a good bond both in the dry state and after water soaking. Because the tensile grips on the ABES did not hold the water-soaked specimen well enough, we modified our Instron jaws to hold the thin ABES samples. (We have been informed that the ABES manufacturer does, however, now provide grips capable of pulling wet wood samples so the entire test could be done on an ABES unit). To provide consistency, we measured both ambient and water-soaked samples on the Instron. For these ABES experiments, we used eastern pine with adhesive applied to only one surface and a 120°C bonding temperature for a closer simulation of what is done commercially with UF-bonded interior plywood and our sample preparation of the three-ply plywood for the HP-1 test. The data in Fig. 1 show that when the ABES-tensile wet strength values were high enough (above the box), the adhesive also passed the standard decorative plywood test (HP-1), but when the shear strength values were too low (below the box), it did not pass the plywood test. Those strength values in the boxed area were marginal in performance. Numeric strength values are not given because the comparative testing discussed later in this paper showed that target strengths are dependent upon the particular adhesive system and wood species used in the test. This new test method has been useful in developing soy flour adhesives that pass the decorative plywood water-soak test HP-1 but may be less predictive with other adhesive systems.

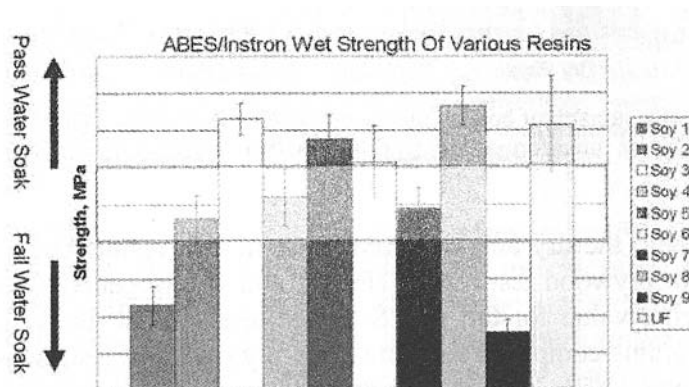


Fig. 1. Comparison of wet tensile strength using the ABES unit for soy-bonded eastern white pine veneers to pass-fail criteria of the HP-1 test method using a similar veneer. Different experimental soy formulations were used and compared with a commercial urea-formaldehyde adhesive.

After our initial work with soy, we thought that this test might be of general utility. Thus, we set up a program to compare the performance of several adhesives on the ABES-tensile test against both the interior and exterior plywood tests. We selected poly(vinyl acetate), urea-formaldehyde, melamine-urea-formaldehyde, and phenol-formaldehyde adhesives to bond both maple and pine using 0.8-mm veneer for the ABES-tensile and 3.2-mm veneer for the interior and exterior plywood tests. Results of the ABES-tensile wet test did not correlate to those of the HP-1 interior plywood test as well as our initial work with soy adhesives had led us to expect (comparing the data in Figs 2 and 3 for each adhesive). For example, the PF with pine had higher shear strength on the ABES-tensile wet test than did the MUF with maple, but the latter combination had a greater percentage pass using the HP-1 test than did the former. There are two possible reasons: (a) the ABES samples, with their smoother surfaces, were less sensitive to an adhesive's holdout on the wood surface (limited penetration into the wood) than were samples in the plywood test, which used a rougher veneer, and (b) we are comparing the results of essentially a shear test with the ABES-tensile test with the plywood test that involves normal forces (delamination) as well as shear forces.

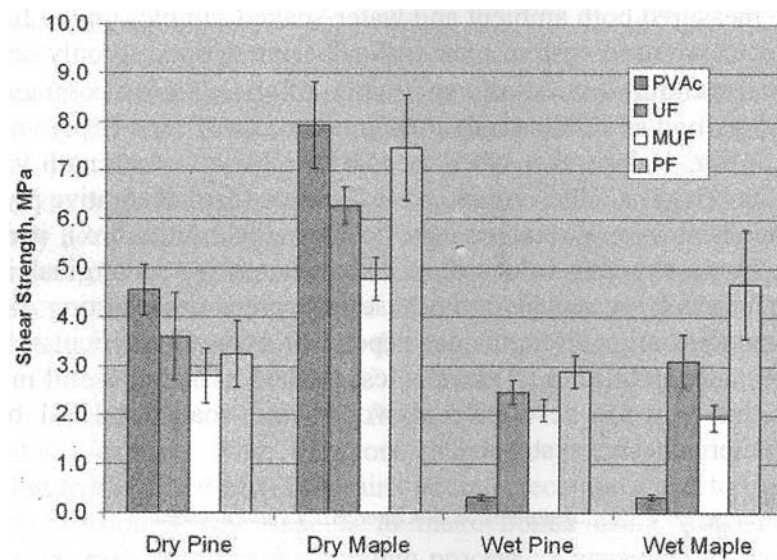


Fig. 2. Dry and wet tensile strength of bonded pine and maple veneers on the ABES unit. The adhesives were poly(vinyl acetate) (PVAc), urea-formaldehyde (UF), melamine-urea-formaldehyde (MUF), and phenol-formaldehyde (PF).

On the other hand, the dry and wet ABES-tensile test results correlated well with the dry and wet exterior plywood test results (Figs 2 and 4). In general, both tests are tensile shear tests; the higher value for the ABES-tensile test is most likely because it tests two plies with parallel grains compared with the three-ply plywood test, which includes a cross ply in the center layer. Thus, the ABES-tensile test could be a means to screen adhesives for exterior plywood applications, as shown by the correlation in Fig. 5. Again, one needs to be careful because the holdout of the adhesive becomes more critical with veneer that

has a rougher surface. Furthermore, temperature, time, moisture, and pressure differences can also be more critical factors comparing species of different penetrability.

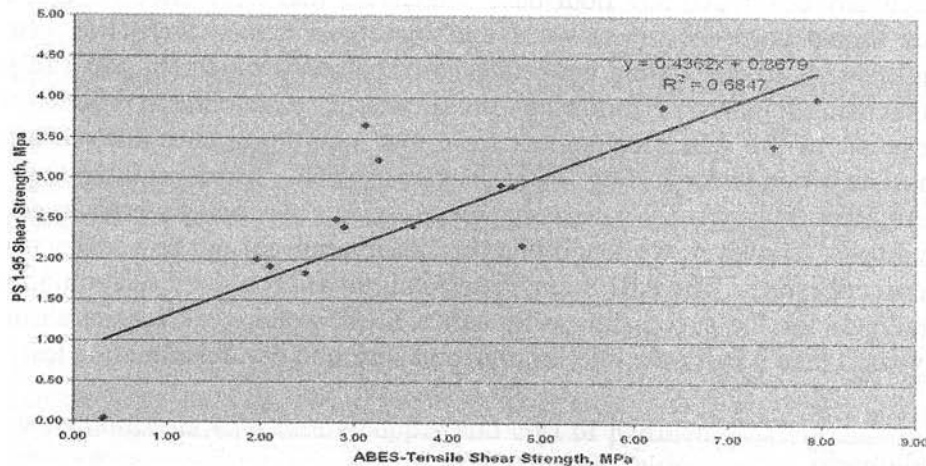


Fig. 3. Pass-fail results of the interior HP-1 test method using a similar type of veneer as used in Fig. 2 bonded with poly(vinyl acetate), urea-formaldehyde, melamine-urea-formaldehyde, and phenol-formaldehyde.

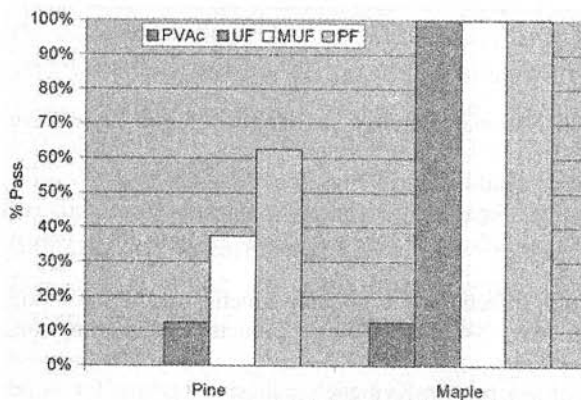


Fig. 4. Dry and wet tensile strengths of bonded plywood (three-ply) using pine and maple veneers and tested by a PS 1-95 test method. Adhesives were poly(vinyl acetate), urea-formaldehyde, melamine-urea-formaldehyde, and phenol-formaldehyde.

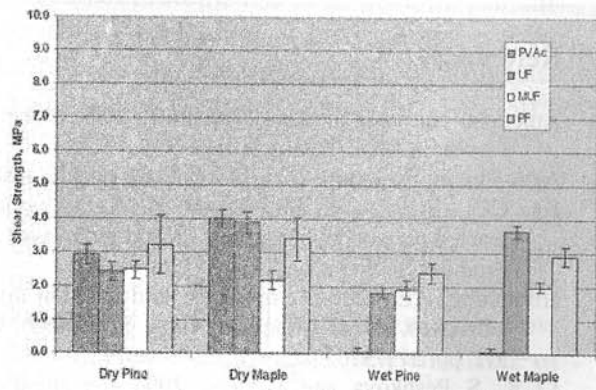


Fig. 5. Comparison of wet tensile strength of bonded veneers on the ABES unit (Fig. 2) with the pine and maple plywood data (Fig. 4). Adhesives were poly(vinyl acetate), urea-formaldehyde, melamine-urea-formaldehyde, and phenol-formaldehyde.

This study also showed, surprisingly, that an adhesive might do quite well in the exterior plywood durability test but not do as well in the interior plywood durability test, as is most clearly visible when comparing adhesive performance data on pine and maple, comparing the data in Figs 3 and 4 (wet strength). Good performance in the exterior test often leads to the expectation of the adhesive passing the interior plywood test. This, however, is not always the case. Swelling forces that can build up in the HP-1 standard protocol apparently can be quite large, and the HP-1 testing can involve normal as well as shear forces, whereas the PS-1 is mainly shear forces.

Summary

We previously developed soy flour-based adhesives that were effective as face resins for oriented strandboard; however, we found that these resins were less effective as plywood adhesives. In developing new adhesive technology for the bonding of plywood, we found that using standard performance tests slowed our development process. Thus, we extended our use of the ABES equipment from just monitoring cure rates to a means of making consistent bonds for testing water-soak resistance. More rapid testing with the ABES-tensile test allowed us to screen resins before spending more time running standardized tests. However, we found that this observation for our soy adhesives was not general for all adhesives. The ABES-tensile test still provides a good screening tool and is a better predictor for the successful performance in the water-soak tensile shear test for exterior plywood than it is for the interior plywood soak and dry delamination test.

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