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Wood Bonding by Surface Reaction

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Chemical bonding is a technique which attempts to involve chemically the surface of wood in the joint formation process. In this research, an attempt has been made to improve overall board properties while at the same time make the whole process more practical from a large-scale application point of view. Accordingly, a 50 weight % solution of nitric acid was applied to green Douglas fir flakes which were dried in a laboratory flake dryer after various time periods. The variables considered included contact time between acid and flakes before drying, time between drying and application of a gap-filling mixture, and total assembly time. Board properties determined were internal bond (IB), modulus of rupture (MOR), modulus of elasticity (MOE), and wet modulus of rupture (WMOR).

Results showed a substantial improvement in board properties compared to boards made utilizing previously reported techniques. Boards which were dried after acid treatment showed a 55% improvement in IB, an 8% improvement in MOE, and a 10% improvement in WMOR, with no change in MOR compared to control specimen values.

INTRODUCTION

The chemical bonding of wood is an interesting and potentially valuable nonpetrochemical alternative to the conventional method of bonding, which uses familiar adhesives such as phenol- or urea-formaldehyde resins. Chemical bonding strives to involve chemically the wood components on the surface of wood in the bonding reaction. Thus, the goal of chemical bonding is to use covalent bonds from adherend to adherend for the total span of the joint. Chemical bonding is achieved by treating wood surfaces with a material which predisposes the wood surface to further reaction, either with wood or with a gap-filling material. Typically, the surface treatments are of an oxidizing nature, with materials such as nitric acid or hydrogen peroxide most

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commonly used. The work reported here will review some of the past history of chemical bonding of wood and discuss recent observations regarding the effects of heat and assembly times on bonding efficiency.

Particleboard was selected as the preferred substrate form for several reasons. Chemical bonding, as it was practiced in this research, required the presence of a wood substrate. By themselves, the components which make bonding possible do not cure or polymerize to form a solid which can be analyzed independently of the wood, *i.e.* the wood surface is a required component in the chemistry leading to joint formation. Earlier work¹ has shown that wood in a solid form is not necessarily the optimum material to use when studying chemical bonding. Wood particles can be randomized throughout a sample so that variations in wood substance can be uniformly dispersed. This approach acknowledges the fact that no two pieces of wood are alike in terms of grain and/or possible chemical surface qualities which make cross-comparisons on a statistical basis difficult.

REVIEW OF LITERATURE

The chemical bonding of wood is not new. Reports of various researchers going back to 1945 have been noted.² Reviews on the topic are available.^{3,4} One approach not covered in the previously mentioned reviews is that of Emerson.⁵ This work involved the treatment of wood with a strong mineral acid such as nitric or hydrochloric acid, followed by the application of a mixture of lignosulfonate, urea, and furfuraldehyde. This technique for wood bonding, known as the Emerite process for the production of "cultured wood", was developed to the point that a plant utilizing this process was built to produce panels for the furniture industry.⁶ This process is very interesting because it is surprisingly similar, in philosophy and materials, to the research reported here. The research presented in this report was developed without prior knowledge of the Emerite process.

PROBLEM DEVELOPMENT

In a previously reported study,³ it was shown that flakeboards can be made by first treating dry wood with 1.5% nitric acid (as a 40 weight % solution), and then applying an aqueous gap-filling mixture of 4.2% ammonium lignosulfonate (ALS), 1.8% furfuryl alcohol (Foh), and 1% maleic anhydride (MA), all of these values based on the oven dry (OD) weight of the wood. This solution was prepared at 50% total nonvolatiles concentration. In

this study, the importance of acid assembly time, pot life of the gap-filling mixture, and total assembly time were discussed.

Acid assembly time, a key parameter of this work, was defined as the time between application of a fine spray of the acid onto dry wood and the application of the gap-filling mixture. The approach taken was to use a fairly strong acid and very dry wood [less than 2% moisture content (MC)]. This was considered desirable because in a direct comparison between 25% and 40% acid, the higher strength oxidizer yielded boards with higher strength values. Other boards were prepared with acid concentrations up to 72% on dry wood with similar trends being noted. The assumption was made that the stronger the acid concentration on the wood surface, the more effective the wood joint. Consistent with this assumption was the fact that very dry wood was used since wood, at an MC greater than 2%, would add substantial water, diluting the acid applied to the wood. Further, with the application of both acid and the aqueous gap-filling mixture, normally as a 50% solids solution, the total MC of the flake mat going to the press was quite high (12% OD basis). This made it difficult to press the boards at 350°F without generating a large number of steam blows. This approach to the manufacture of chemically bonded boards yields panels of good strength and stability. However, it should be noted that drying and maintaining wood at 2% MC is quite difficult, energy intensive, and not at all practical for large scale flakeboard manufacture.

A new approach which would lead to the development of good bonding and be more conducive to large-scale manufacturing techniques was considered desirable. Thus the current research was undertaken.

EXPERIMENTAL

Nitric acid was applied to wood at a high MC, typically in the range of green wood, and the wood was then dried in a normal manner. Three time factors were defined for this project. The first, T1, was the assembly time between the application of the acid and drying of the wood. The second time parameter, T2, was the assembly time between the removal of the treated wood from the dryer and the application of the gap-filling mixture. The last time factor, T3, was the assembly time between the application of the gap-filling mixture and hot pressing. The experiment evolved as follows.

Dry Douglas fir flakes were used. They were prepared in a ring type flaker set to produce flakes 13 mm by random width by 0.38 mm thick. After equilibrating to room MC, classifying to remove the fines, and randomizing, the flakes were stored in tightly sealed polyethylene bags until needed. As required for the experiment, flakes were blended with sufficient water to yield an MC of 50%, bagged for three hours in tightly sealed polyethylene bags, and

then sprayed with a 50% solution of nitric acid using a 1.5% nitric acid, OD wood basis. The times for T1 were set at 0, 2, and 24 h. After drying to an MC of 5% in an 80°C rotary dryer, the flakes were sprayed with the gap-filling mixture previously defined, with T2 times of 0, 24, and 72 h. The nonvolatile component of the gap-filling mixture was 7%, OD wood basis. Finally, boards were pressed with T3 times of 0, 2, or 24 h. All boards were pressed to a target density of 0.75 g/cc and a target thickness of 12.7 mm in a 177°C press. The press schedule called for a total press time of seven minutes, which included one minute to stops.

Two types of control boards were prepared. The first was based on the application of nitric acid to dry wood in the manner previously reported,³ with a T1 time of two hours, a gap-filler pot life of two hours, and a T3 time of two hours. The second set of controls was prepared with 6% phenol-formaldehyde particleboard resin, OD wood basis.

After the statistical analysis of this main body of experiments, two other sets of boards were made. The first set of boards, at the observed relative optimum of 0 h wet assembly time, 72 h dry assembly time, and 0 h total assembly time, was made with acid-sprayed wood dried at 49°F instead of at 80°C used previously. Finally, the last set of boards was prepared using the same assembly time schedule as the above set, but with aspen flakes dried at 80°C. Four replications for each experimental variable or control factor were made—a total of 124 boards.

Testing consisted of the determination of IB, tensile strength perpendicular to the face, modulus of elasticity, modulus of rupture according to ASTM D-1037, and the determination of wet modulus of rupture, which is defined as the MOR after a two-hour boil followed by a one-hour cold soak with all calculations based on dry dimensions. Statistical analysis included analysis of variance, with the Duncan's New Multiple Range Test to identify significant values, with 1% used as the minimum level of significance.

RESULTS AND DISCUSSION

The experimental design and complete results of the experiment are reported in Table I.

Main effects

There are three possible main effects with the experimental design. The T1 time results are shown in Table II. Both IB and WMOR decreased with increased T1 time. Such parallel behavior did not occur with the T2 assembly time (Table III) because the WMOR decreased with increased T2 time, and the IB

TABLE I
Experimental design and summary of data

T1 Assembly time (h)	T2 Assembly time (h)	T3 Assembly time (h)	MOR MPa	MOE MPa	IB MPa	Wet MOR MPa	
0	0	0	11.56	3330	0.44	1.60	
		2	11.65	3247	0.65	1.70	
		24	11.52	3323	0.54	1.73	
	24	0	0	9.82	2875	0.43	1.54
			2	11.82	3854	0.52	1.50
			24	12.00	3516	0.61	1.43
		72	0	11.57	3406	0.64	2.03
			2	11.49	3537	0.52	1.27
			24	11.20	3599	0.45	0.92
	2	0	0	10.80	3172	0.54	2.11
			2	11.82	3475	0.52	1.30
			24	12.26	3689	0.44	0.81
24		0	0	11.20	3489	0.56	1.10
			2	11.85	3716	0.50	1.13
			24	11.49	3696	0.47	0.92
		72	0	11.35	3427	0.52	1.33
			2	11.58	3558	0.56	1.02
			24	11.96	3482	0.55	1.05
24		0	0	10.69	3282	0.45	1.66
			2	10.04	3282	0.38	1.27
			24	12.44	3834	0.49	1.24
	24	0	0	10.65	3185	0.46	1.80
			2	10.93	3316	0.44	0.98
			24	12.12	3730	0.54	1.64
		72	0	11.81	3454	0.61	0.96
			2	12.52	3585	0.54	0.92
			24	11.19	3620	0.43	0.72
	0	72	0†	13.99	3606	0.42	2.21
	0	72	0‡	10.40	2944	0.59	0.70
	Control: Nitric acid			11.48	3151	0.41	1.85
Control: Phenol formaldehyde			24.21	2972	1.06	10.24	

† Aspen dried @ 80°C.

‡ Douglas fir dried @ 50°C.

TABLE II
Main effects: board properties as a function of T1 assembly time

	T1 time in hours		
	0	2	24
MOE MPa	3406	3516†	3461
MOR MPa	11.40	11.59	11.38
Wet MOR MPa	1.52†	1.21	1.24
IB MPa	0.54†	0.52†	0.48†

† Identifies which values are significantly different from all other values of the same property @ 1% level.

TABLE III

Main effects: board properties as a function of T2 assembly time

	T2 time in hours		
	0	24	72
MOE MPa	3516	3482	3392†
MOR MPa	11.42	11.31	11.63
Wet MOR MPa	1.50†	1.35†	1.14
IB MPa	0.50	0.50	0.54†

† Identifies which values are significantly different from other values of the same property @ 1% level.

TABLE IV

Main effects: board properties as a function of T3 assembly time

	T3 time in hours		
	0	2	24
MOE MPa	3268†	3503†	3606†
MOR MPa	11.05	11.52	11.80†
Wet MOR MPa	1.59†	1.23	1.15
IB MPa	0.52	0.52	0.50

† Identifies which values are significantly different from all other values of the same property @ 1% level.

increased with T2 time. In this latter case, the MOE paralleled the behavior of the WMOR.

Table IV shows the effect of T3 time on board properties. IB was not significantly influenced by the total assembly time. The results are interesting because both the MOE and the MOR increased with increased total assembly time, while the WMOR decreased with increased total assembly time.

Two-factor interactions

Figure 1 shows the dual effects of T1 time and T2 time on the wet and dry MOR. There were no significant interactions for the dry MOR, while the WMOR of the boards pressed after a T2 time of 72 h and a T1 time of 24 h had a significantly lower wet bending strength. The effects of T1 and T2 times on the IB are shown in Figure 2. These data show that a T2 time of 72 h can eliminate the effects of T1 time. This is in contrast to the WMOR, where an extended dry assembly time dramatically reduced wet bending for the 24-h wet assembly time.

The T3 time factor did not demonstrate any significant two-factor interactions.

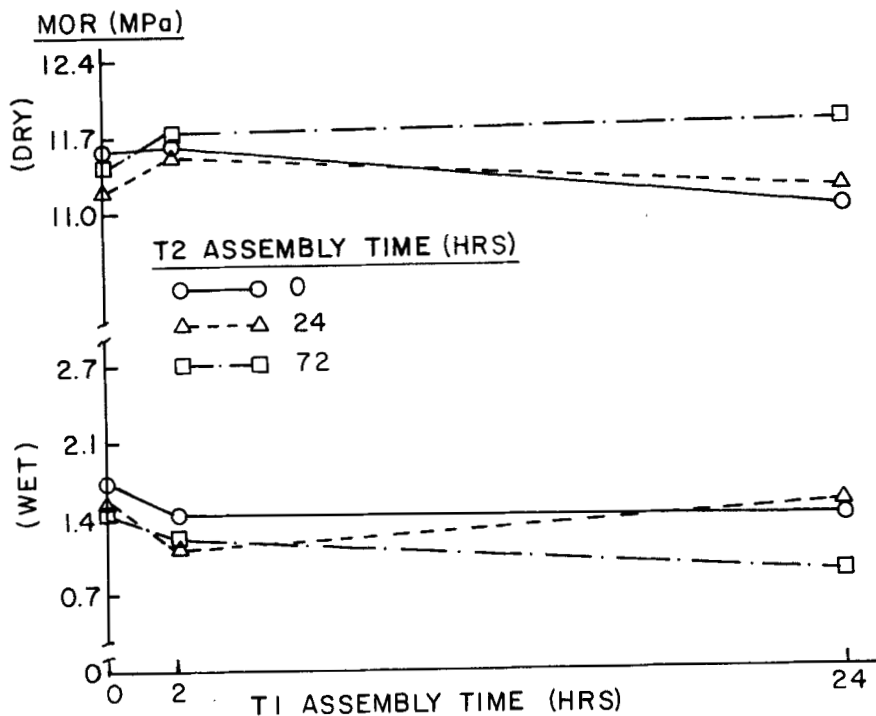


FIGURE 1 The dual effects of T1 time and T2 time on the wet and dry MOR.

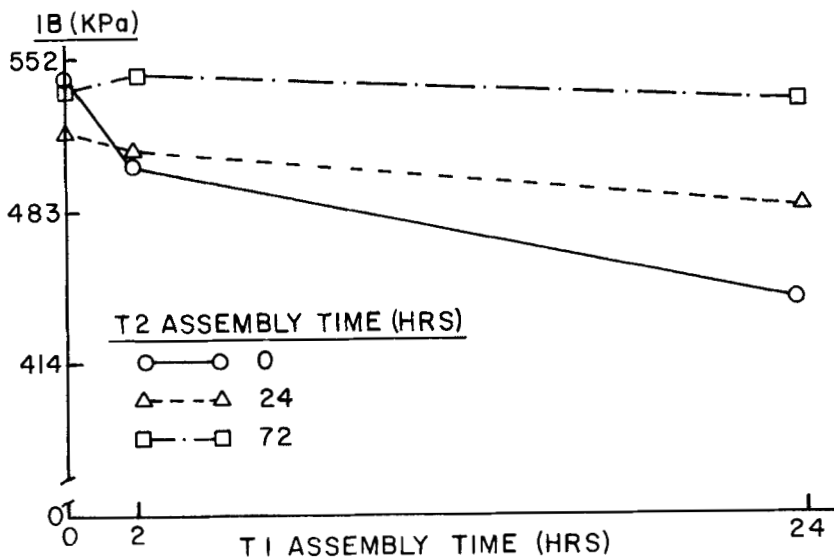


FIGURE 2 The effects of T1 and T2 times on the IB.

Three-factor interactions

Every board property investigated showed significant three-factor interactions. The interpretation of these interactions will probably remain unknown until the chemistry of this bonding system is better understood and the nature of each individual factor can be documented. Discussion of three-factor interactions must therefore be postponed until such time as it is possible to work from a position of greater knowledge.

Other interactions

In reviewing the results shown in Table I, several combinations of assembly times identify a high level of bonding. One such combination includes a wet assembly time of 0 h, a dry assembly time of up to 72 h, and a total assembly time of 0 h. Based on the relatively high values of both IB and WMOR, this particular combination was selected for two side tests.

The first of these was dryer temperature. Previously unpublished data suggested that dryer temperature might be a factor in generating an activated surface for the development of good bonding. Keeping all other factors constant, one batch of flakes was dried to the same MC level (5%), but at 49°C instead of 80°C. This, of course, required a somewhat longer exposure to the lower heat. The results are presented in Table I. While board properties during dry tests were roughly parallel to those of boards processed from 80°C dried flakes, the wet properties dropped off to approximately 1/3 the value of the higher temperature treatment.

In an earlier report,³ an attempt was made to make boards without the use of the acid pretreatment, *i.e.* relying solely on the gap-filling mixture to provide the bonding. As reported, the boards had adequate dry strength values, but completely fell apart when brought into contact with water. These results parallel the effect of temperature reported now. Drying at elevated temperature does cause a change in the surface of the wood, which when treated with the gap-filling mixture can develop a water resistant bonding when pressed with heat into a panel. Since all other factors in board preparation were held constant, it must be assumed that drying temperature is a key factor in activating the surface of the wood. It is not known at this time whether lower temperatures yield fewer active sites for bonding or, alternately, whether higher drying temperatures yield fundamentally different types of functional groups on the surface of wood.

The use of aspen was included to see if a hardwood had the potential for bonding with surface reactions similar to those observed with softwoods. No attempt was made to optimize the stoichiometry or assembly time factors for the aspen furnish. Aspen, with its well documented differences in both lignin

and hemicellulose chemistry, had the potential to point out if very specific reactions were taking place with the Douglas fir which could not take place with substrates of different chemical makeup. While the aspen was flaked through the same ring flaker, its mechanical differences yielded flakes with a different character and a higher percentage of fines than the Douglas fir used for the main body of the experiment. As shown in Table I, the aspen did yield a board of broadly comparable properties. The only property which was lower was the IB. This suggests that the application of chemical bonding technique to other species may not involve any major changes in a technique that is comparable to the approach taken here.

In previous work, a characteristic of the chemical bonding process was the relatively high MOE relative to other properties. In this work we see a similar trend. The phenol controls show MOR, IB, and WMOR values all substantially higher than those for the chemically bonded board. In contrast, the phenol-formaldehyde bonded board yielded one of the lowest MOE values listed in Table I, fully 29% lower than the highest chemically bonded value. This phenomenon reflects the nature of the bonding system being used.

When a regular film-forming resin such as phenol-formaldehyde is used at the rate of 6% solids OD wood basis, the predominant material in the board is wood. This wood, in the form of flakes, is thought to be simply spot-welded together, as the amount of resin is far below the amount necessary for complete coverage. The physical properties of the board are controlled by the geometry and orientation of the wood flakes, which are produced from unmodified wood material. Chemically bonded wood has been subjected to a fairly severe surface oxidation. The wood has been chemically modified and no longer represents wood as found in the tree. One of the characteristics of oxidized wood is "embrittlement". This embrittlement leads to an increase in flake stiffness and therefore board stiffness, as reflected in the higher MOE values seen in Table I.

Under acidic conditions, wood can be expected to undergo certain fundamental changes. The lignin fraction of the wood is normally expected to condense into higher molecular weight fractions, while the carbohydrate fraction is thought to hydrolyze to more soluble material. The acid conditions employed for chemical bonding are not so severe as to make all the sugars soluble, and one probable reaction sequence would suggest that 5-carbon sugars are chemically modified so as to produce furfuraldehyde, a precursor to furan resins.

This concept has led one researcher⁷ to base an approach to particleboard manufacture on the *in situ* production of furan type binders by applying oxidizers, furfuryl alcohol, and sucrose. It can be assumed that the *in situ* manufacture of furan type polymers probably plays some role in any wood bonding process which includes surface oxidation. The characteristic stiffness

of polymeric furan materials probably also contributes to the high MOE seen in Table I.

The nature of the bonds which are formed is not known. It is assumed that the formation of carbonyl groups plays a key role in the effectiveness of the nitric acid pretreatment. These carbonyl groups can be in the form of organic acids, aldehydes, and ketones. In an attempt to understand the relationship between bonding and wood chemistry, Jahan-Latibari⁸ investigated the strength of chemically bonded boards as a function of the bound and soluble acid content of the wood after pretreatment. No correlation was found. This seems to suggest that the reactive groups closely related to bond development are aldehydic. Work is currently underway to investigate this possibility.

There is considerable information available concerning the oxidation of both the lignin and the carbohydrate fractions of the wood. Excellent reviews are available for each.^{4,9,10} The problem is in interpreting the cause and effect relationships between the bonding treatments, such as T1 and T2 assembly times, and the specific changes in components of the wood or on wood mechanical behavior. Until such time as the surface chemistry of wood can be quantified before and after various treatments, the problem of understanding the pathways to bond development will still exist. This does not imply that progress cannot be made. The data presented here show the results of a direct effort to improve bonding, while at the same time modifying the techniques to resemble more closely an industrial approach to board manufacture.

One of the key developments of this study involves the effective strength of the acid used to pre-treat the wood. In unpublished work, acid concentrations up to 72% were applied to dry wood. When the amount of water present in wood, even at low MC levels, is included in the calculations, the effective acid concentrations normally found are in the range of 35%. For the work reported here, the effective acid concentration present on the wood surface is 2.8%. These observations suggest that the history of the wood, with respect to moisture content and heat exposure, is far more critical than the working concentration of the pre-treatment acid. To this end, future research should be directed toward studying the effect which heat and moisture have on the effectiveness of any pre-treatment technique as a standard screening process.

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