HOW OVERDRYING WOOD REDUCES ITS BONDING TO PHENOL-FORMALDEHYDE ADHESIVES: A CRITICAL REVIEW OF THE LITERATURE. PART II. CHEMICAL REACTIONS

Alfred W. Christiansen

Chemical Engineer
USDA Forest Service
Forest Products Laboratory[1]
One Gifford Pinchot Drive
Madison, WI 53705-2398

ABSTRACT

Literature dealing with the effect of excessive drying (overdrying) on wood surface inactivation to bonding is reviewed in two parts and critically evaluated, primarily for phenolic adhesives. Part 1 of the review, published earlier, covers physical mechanisms that could contribute to surface inactivation. The principal physical mechanism is the migration to the surface of extractives that decrease wettability. Pan II of the review considers mechanisms involving chemical reactions: reduction of wood surface strength, oxidation and pyrolysis of wood bonding sites, and chemical interference with resin cure or bonding. In those cases where extractives are not the primary cause of inactivation, oxidation or pyrolysis probably is the major cause of inactivation. Inactivation of oak and of some Southeast Asian hardwoods may be due to the acidity of extractives, but the importance of decreased wettability caused by extractives cannot be dismissed.

Keywords: Drying, inactivation, adhesive, bonding, review, extractives, mechanism, wettability, oxidation, acidity.

This is the second part of a critical literature review that deals with the ways in which excessive drying (overdrying) causes wood surfaces to be "inactivated" to bonding. Part I (Christiansen 1990) covers general aspects of wood surface inactivation and reviews these physical mechanisms by which overdrying weakens bonding. The three mechanisms are: (1) exudation of extractives to the surface, which lowers the wettability or hides the surface; (2) reorientation of wood surface molecules, which reduces wettability or bonding sites; and (3) irreversible closure of large micropores in cell walls. Part II of the literature review shows how chemical reactions related to overdrying may cause inactivation of wood surfaces to bonding.

POSTULATED CHEMICAL MECHANISMS

The inactivation of wood surfaces was first noted in occasional problems of bonding to plywood surfaces after hot pressing. The original hypothesis put forward by De Bruyne (1939) for the mechanism of inactivation was that water was eliminated from between pairs of cellulose hydroxyl groups to form ether bonds. Ether bonds are not as receptive as the original hydroxyl groups to hydrogen

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bonding with polar adhesives. De Bruyne's hypothesis was based on the earlier hypothesis of Stamm and Hansen (1937) that wood was heat stabilized though the formation of ether bonds. Later, Seborg et al. (1953) showed that crosslinking by ether bond formation was not a good explanation for thermal stabilization; although wood was stabilized against swelling by water, it was not stabilized against pyridine or sodium hydroxide, none of which would break ether bonds.

Reduction of surface strength

Although the chemical means for degrading the strength of wood surfaces are almost certainly oxidation and pyrolysis, many published works do not refer to actual chemical mechanisms. In this section, I review the literature that has primarily focused on the decrease of mechanical properties rather than on the degradative process itself or the decreased number of surface bonding sites.

High temperature effects on wood strength

Northcott (1957) stated that reduced strength of wood surfaces is one factor that tends to produce shallow wood failure. Microscopic examination of specimens that had exhibited shallow wood failure were found to have failed by fracture through the cell walls of the wood, rather than by adhesive failure. Later, however, Northcott and Colbeck (1959) found that exposure of Douglas-fir to a temperature of 191 C for slightly over an hour did not significantly affect the bending strength, or modulus of rupture (MOR), of veneer.

Bending strength is influenced more strongly by surface conditions than are most mechanical properties. So, low wood strength on the surface could not be the cause of the shallow wood failure. Partly as a consequence of this finding, a new hypothesis for surface inactivation, "casehardening," was developed for bond quality degradation (Northcott et al. 1959).

Hare (1 973) found statistical evidence of thermal damage in eastern spruce that had been dried in roller dryers. However, the high wood failures (all above 98%) and the high shear strengths [all averaging above 1.55 MPa (225 lb/in.²)] observed for specimens dried in any of three types of dryers or air dried at room temperature indicate to me that none of these specimens were significantly inactivated to bonding.

For solid wood, Stamm (1956) estimated that over 30 min of heating in air at 200 C were required for softwood specimens to lose 10% of their original MOR, as well as 1% of their weight. The degradation rate was faster under saturated (pressurized) steam conditions. The rate was slower when oxygen was excluded from the heating medium. Stamm noted that Douglas-fir hemicellulose degraded about four times quicker than whole wood.

Several physical and mechanical properties of loblolly pine were measured after heating specimens at 150 C for times up to 16 h in environments of nitrogen, air, or oxygen within small airtight cylinders (Mitchell 1988). Initial moisture contents (MC) of samples put in the cylinder were either 0%, 12%, or that of the green condition. Trends of MOR values for the specimens were nearly the same after heating in air or nitrogen, the percentage values for retained MOR for specimens heated in air averaging only slightly less than for those heated in nitrogen. After 12 h heating, the MOR had decreased insignificantly at 0% MC, decreased to about 80% of unheated controls at 12% MC, and decreased to around 63% of

controls for initially green wood. The degradation was attributed to hydrolysis reactions. At 150 C, therefore, heating wood in a normal atmosphere has almost no more degradative effect on the MOR than heating in nitrogen, especially when compared to the effects of moisture content on MOR.

Hillis (1984) has reviewed the effect of high-temperature drying on the hygroscopicity and strength characteristics of wood, primarily lumber. A major factor in these property changes may be hemicellulose losses or conversions.

Davis and Thompson (1964) exposed 15.9-mm-($^5/_8$-in.-)square sticks of southern pine, southern red oak, and Douglas-fir to temperatures of 150 C, 175 C, and 200 C for 20 to 60 min. After 20 min at 200 C, these species had lost 20 to 30% of their toughness, compared to controls. Researchers found that changes in toughness, whether in these oven-heating experiments or in low-temperature steam-heating experiments, were significantly related to the loss of hemicellulose, which is a major component of wood and is the most heat sensitive.

Stamm et al. (1946) showed that toughness and MOR of western white pine decreased and dimensional stabilization increased after heating at increasing temperatures between 100 C and 320 C for various fixed times. The samples were heated in molten metal baths to exclude oxygen. Stamm et al. (1946) found that the reaction time needed to obtain a certain level of dimensional stability approximately halved for each 10 C rise in temperature.

Seborg et al. (1953) found that oxygen was not necessary for dimensional stabilization of wood when heating at 300 C. Although wood lost 20% of its weight by heat treatment, reduced hygroscopicity and dimensional changes did not depend on the composition of the heating medium. The great losses in toughness, abrasion resistance, and shear resistance were apparently not due to oxidation.

Troughton and Rozon (1974) investigated the loss of tensile strength, ultimate tensile strain, and work to rupture during different types of heat treatments for Douglas-fir earlywood and white spruce. Thickness of the pieces was only 100 μ, in order to simulate surface conditions throughout the pieces. A temperature of 200 C was used for oven heating, hot-press drying, and silicone oil bath heating. Steam heating took place in a pressurized bomb at 183 C, generally at 1.07 MPa (10.6 atm) (saturated steam). For one group of spruce specimens, the pressure was 0.27 MPa (2.7 atm) (superheated steam). Heating in the oil bath was the least detrimental, causing the slowest decline of properties. Heating in the oven or in the hot press decreased the properties at faster rates than did heating in the oil bath. Decreases in properties often had similar rates in the oven and the hot press. Properties were most quickly degraded by heating in saturated steam. Starting from a common vacuum-dried state, the tensile strength of Douglas-fir heated by either oven or hot press for 10 min dropped by an average of 45%, whereas white spruce strengths dropped only 3% under the same conditions. Generally, average strength values for spruce fell slower than did those for Douglas-fir, and the differences among average strengths of spruce specimens after the oil bath, oven, and hot press heating treatments were much less than those for Douglas-fir. Interestingly, for the spruce specimen heated 40 min at 183 C under superheated conditions (much below saturation), properties fell at a rate very close to rates for oven-heating at 200 C for 40 min. No estimate of variability was provided.

Troughton and Rozon reasoned that the species differences were due to spruce

containing both earlywood and latewood, whereas the Douglas-fir contained only earlywood. Although the authors attributed the less degradative effect of the oil-bath-heated specimens to the exclusion of oxygen from the sample, they thought that the hot pressed sample must have contained sufficient oxygen to create conditions similar to those of a forced air circulating oven. The severe degradation for saturated steam heating was attributed to hydrolytic degradation. These results indicate that heating wood at high temperatures strongly degrades the surface strength.

Suchsland and Stevens (1968) devised a useful analysis for determining whether wood strength or bondline strength is the cause of bond failure. The analysis uses a plot of wood failure against plywood shear strength for veneers dried at various conditions, including several inactivating conditions. Reductions of wood strength should increase wood failure and reduce shear strength. Reductions of adhesive bond strength should reduce both wood failure and wood shear strength, and also increase the negative slope of the regression line between bond strength and wood failure. Applying such an analysis to unextracted veneer dried to a surface temperature of 260 C, the researchers concluded that bondline strength, not wood strength, accounted for the lower values of plywood strength.

High-temperature effects on strength of other cellulosic materials

Dry heat treatment of hardboard results in losses in several mechanical properties and a decline in the degree of polymerization of cellulose (Back and Klinga 1963). For paper, as steam temperatures for drying pulps were increased to 200 C, several properties of sheets made from the pulps declined and the degree of polymerization of cellulose fell (Stockman and Teder 1963).

Overdrying has detrimental effects on the strength of cotton. Heating cotton caused little strength loss up to 160 C, but rapid deterioration occurred above this temperature (Brushwood 1988). Compositional changes of cotton heated at high temperatures included rapid increases in the amount of low molecular weight reducing sugars at temperatures above 140 C. Cotton started to yellow after 20 min at 120 C, but in only 10 sec at 200 C.

Oxidation and pyrolysis

Evidence for oxidative inactivation

Spectroscopic evidence for oxidation of wood surfaces. – Chow (1 97 la) used infrared spectroscopy to follow chemical changes occurring in wood during isothermal heating. The experiments used 30-µm-thick sections of white spruce earlywood. These specimens were heated in an atmosphere-controlled chamber in an infrared spectrometer. The beam passed continuously through the sample, and transmission spectra were obtained intermittently without removing specimens from the chamber. The samples were essentially the thickness of one earlywood tracheid, and would have reached the temperature of the surrounding atmosphere almost instantaneously. Temperatures from 100 C to 240 C were used. After each specimen was inserted into the heated atmosphere, the intensity of the infrared band at 1,730 cm^{-1} was monitored. The intensity of this band, which for wood is primarily due to ester and carboxylic acid functional groups, decreased for a period of time, and then increased. The period during the decrease

was attributed to loss of the ester and carboxyl groups, which in native wood occur primarily in the hemicellulose; the later increase was attributed to oxidative carboxylation of hydroxyl and aldehyde groups, which occur in all the major wood components. The time at which intensity of the 1,730 cm^{-1} band reached a minimum was taken as the time at which significant oxidation began to occur; I will refer to this as the characteristic oxidation time. As the temperature of heating increased, this characteristic oxidation time decreased. The characteristic oxidation time was longer when the atmosphere around the sample was nitrogen instead of air, though pure nitrogen gas could not cause the oxidation. Chow speculated that the small number of active hydroxyl groups that would otherwise be available for covalent bonding to phenolic resin are selectively consumed in carboxylation reactions during high temperature drying.

The characteristic oxidation time for native (unextracted) white spruce heated in air at 200 C occurs at 25 min. However, when wood is extracted with acetone before being heated, this period is increased to 50 min. Chow believed this time difference proved that the extractives played a role in the oxidation process, the fatty acid extractives serving as catalysts in the reactions. However, there are other plausible interpretations. It seems possible that the extractions also removed other components, perhaps simple sugars or some nonsugar extractives, that are more readily oxidized. Extraction of sugars would also be important if the heat and acids had been converting simple sugars to hydroxymethylfurfural, which has a higher oxidation state than wood sugars and is easily converted to dicarbonyl compounds or eventually, as Stamm (1975) puts forward, to water insoluble polymers that would reduce hygroscopicity.

As samples were heated at the higher temperatures, the increasingly narrower gap between behavior measured in the presence of nitrogen and in the presence of air led Chow to think that pyrolysis became the predominant reaction.

Chow and Mukai (1972) correlated thermal degradation of white spruce thin sections (measured by X-ray crystallinity, degree of polymerization of cellulose, and hydroxyl content) to color intensity differences (before and after drying). Chow and Mukai also linked color intensity changes to poor bond quality. Experiments in which veneer surfaces were oxidized using ozone confirmed the deleterious effect of surface oxidation. After wet veneer surfaces were exposed to ozone at room temperature, the plywood made from these veneers showed progressively lower bond strengths as ozone treatment lengthened. Interestingly, dry veneers subjected to ozone gas treatment did not show indications of oxidation in their infrared spectra, nor did the plywood made from this veneer differ in bond quality from control plywood.

Wood bonding evidence for oxidation. – Chow (1971a) reported bonding experiments along with the spectroscopic experiments previously discussed. Veneer 3.2-mm- ($^1/_8$-in.-)thick was dried at temperatures used in the spectroscopic study, and the drying times corresponded to times before and after the characteristic oxidation time found in the spectroscopic study. However, wet veneer put in the dryer (at moisture contents of 40% for heartwood and 150% for sapwood) would have required several minutes before reaching the point where surface temperatures would have reached oven temperatures, because of the cooling effect of surface evaporation. Therefore, the extremely thin samples used in the infrared experiments must have been at the selected temperatures for much longer times
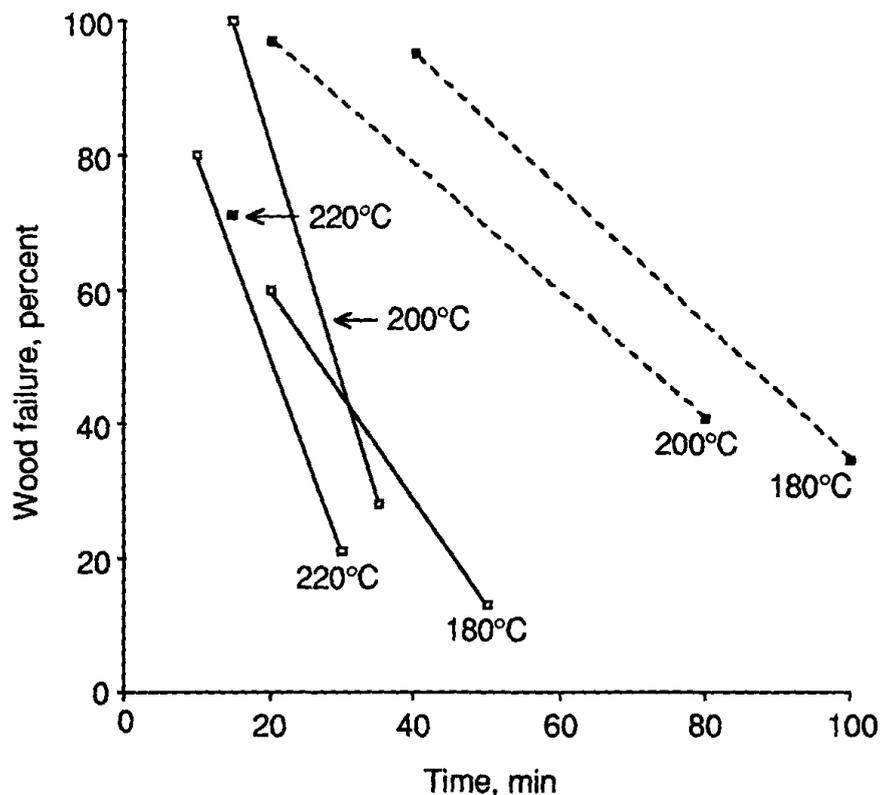
FIG. 1.   Wood failure, after wet testing, compared to drying time for 3.18-mm-thick white spruce sapwood veneer dried in air at the indicated temperatures: control samples (open squares); wood extracted with acetone before drying (filled squares). (Data from Chow 1971a, Tables 1 and 3.)

than were the veneer surfaces used for the bonding experiments. To show changes in veneer bond quality with heating time, Chow chose widely different times at which to take samples (e.g., 15 and 35 min at 200 C). If one plots values from Tables 1 and 3 of Chow's paper (197 la), as in Fig. 1 and Fig. 2, the values for wood failure and shear strength for extracted samples heated at 180 C and 200 C show much less susceptibility to inactivation than control (unextracted) wood at the same temperatures. Such large changes in bond quality would also be expected if the cause of inactivation was a decrease in wettability as a result of fatty acid migration to the surfaces. The differences in wood failure and shear strength values between extracted and unextracted samples heated at 220 C do not show large beneficial effects of extraction, but pyrolysis may be more dominant at such high temperatures. (Each temperature and treatment combination consists of only two time points, not enough to give a feeling for curvilinear relationships commonly seen for drying curves.) Inactivation behavior is evident despite the long pressing time (8 min) chosen to give maximum cure. Chow's use of long pressing times to assure adequate cure contrasts with the work of Northcott et al. (1959), who felt that inactivation on production lines was due to *undercure* of the adhesive during normal pressing times.
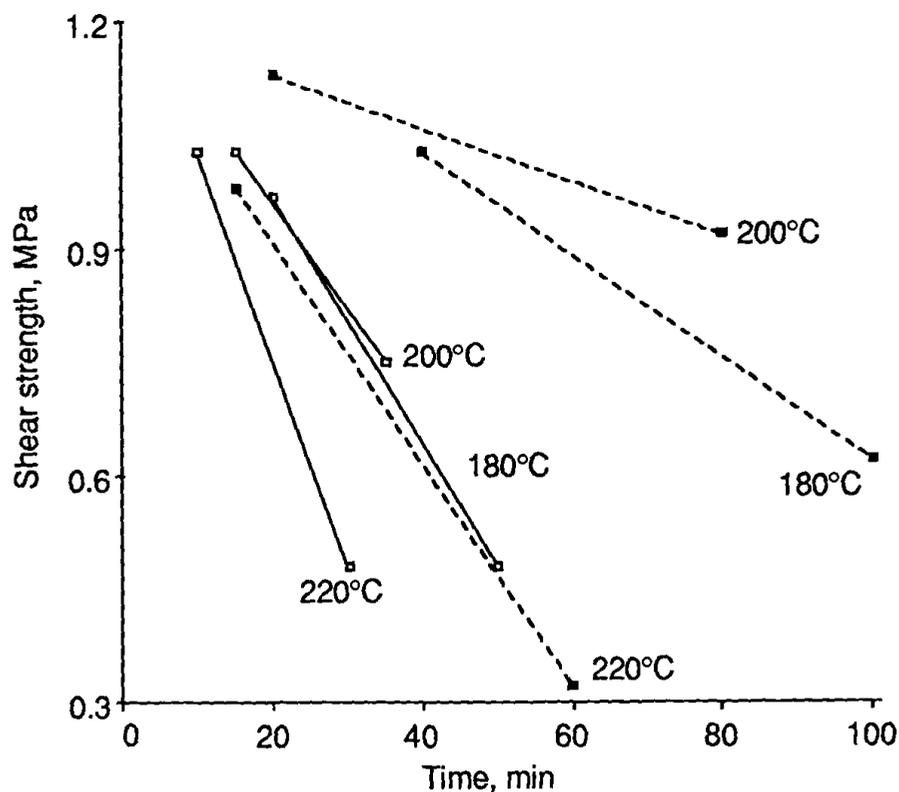
FIG. 2.   Wet shear strength compared to drying time for 3.18-mm-thick white spruce sapwood veneer dried in air at the indicated temperature: control samples (open squares); wood extracted with acetone before drying (filled squares). (Data from Chow 1971a, Tables 1 and 3.)

Chow's Table 5 (1971a) gives bond strength and wood failure data on heartwood veneers heated in nitrogen. When compared with similar data, in his Table 1, for heartwood veneers heated for somewhat different times in air, the trends in the data for shear strength and the absolute values for wood failure indicate that wood in a nitrogen environment is less susceptible to inactivation. This fact strongly supports a role for oxidation in an inactivation process. The exclusion of some oxygen from the drying media (e.g., by use of more burner gases) might also help retard the effects of oxidation. Pyrolytic degradation would still affect inactivation, even in systems where oxygen was excluded.

Chow (1971b) noted that when the fibers are degraded, a weak force is sufficient to pull the fibers apart, and wood failure increases despite the low bond strength. Scanning electron microscopic analysis of a bondline that failed at low strength and low wood failure reportedly showed a cast impression of wood fibers in the glue, indicating good contact of glue with the wood but a lack of chemical adhesion. This evidence indicates interference with bonding between the wood and the adhesive.

Chemical evidence for oxidation. – One further experiment of interest is that illustrated by the data in Chow's Table 4 (1971a), both for panels from veneers
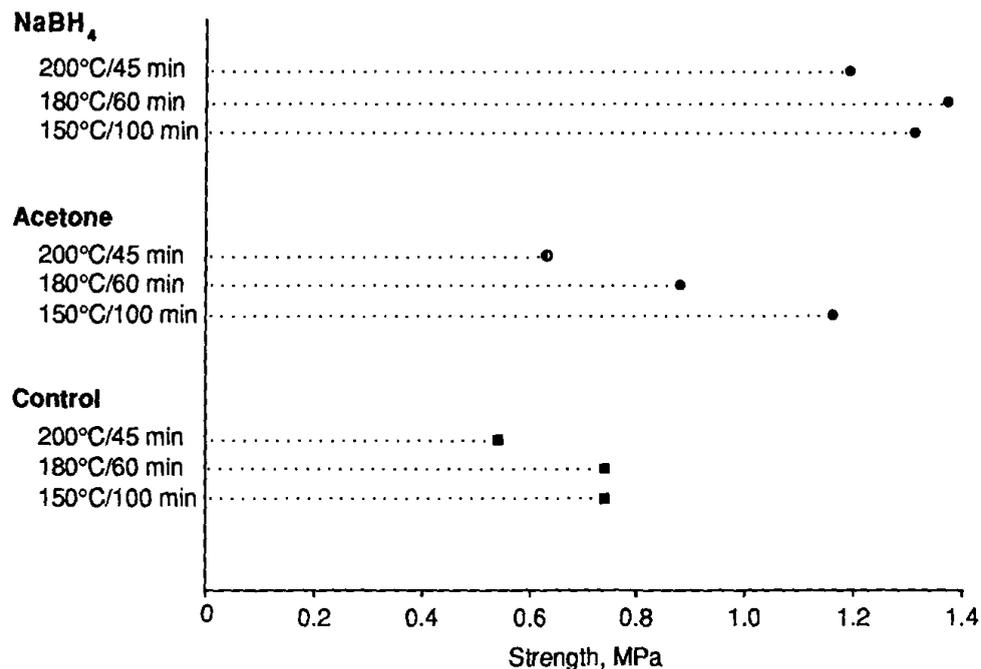
FIG 3. Dry shear strengths of 3.18-mm shear-thick white spruce heartwood veneer. Treatments are listed as headings on the ordinate; NaBH4 indicates wood stabliized with soduum borohydride before drying; Acetone indicates wood that after drying was txtracted whth acetone; Contyrol indicates wood that was dried without other treatment. The drying conditions are repeated under each of those headings. (Data from Chow 1971a, Table 4.)

"stabilized" with sodium borohydride (NaBH₄) (a chemical agent for reducing mainly aldehydes and ketones to hydroxyl groups) and for panels made from veneers extracted with acetone after drying. Panels with both those treatments were compared to controls, which had been made from untreated veneers. Those results are plotted in Fig. 3. The data indicate that the NaBH₄ treatment did produce better bond quality than did the control wood. The amount of cellulose aldehyde groups available for reduction is small, so reduction of aldehyde groups would more likely occur in the lignin or hemicellulose. Ketone groups are an insignificant factor.

However, I can interpret the data in light of previously cited work on fatty acid inactivation. For this interpretation, the samples extracted with acetone after drying provide additional information. At relatively low drying temperatures, where fatty acids might physically adsorb onto the surface but not readily react with it, acetone should be able to extract a portion of the fatty acids, allowing good bonds. At higher temperatures, chemical reaction between fatty acids and wood becomes much more important, and acetone extraction becomes less effective. An interpretation for the effect of NaBH₄ might be that the boards, which were soaked in 0.5% NaBH₄ methanolic solution, have had fatty acid esters on surface cellulose sites reduced back to the fatty acids and hydroxyl groups, allowing the fatty acids to be absorbed into the methanolic solution or later into the phenolic resin. Ester linkages can be reduced by this chemical if a large excess of NaBH₄

is present in the methanol (Finar 1973), which would be the case for reaction with esters on the wood surface in a surrounding solution. Thus the "stabilization" might be a de-esterification of the fatty acid esters.

Oxidation in other lignocellulosic systems. – During several hours of aging at 130 C to 190 C, cellulose is degraded, while carbonyl and carboxyl groups are formed (Hernadi 1977). The number of aldehyde groups formed correspond to the number that would be formed from cellulose chain bond breakage during depolymerization, plus an amount attributed to oxidation of hydroxyl groups. The rate is much faster at higher temperatures, as expected, and at 190 C most of the reaction occurs within the first hour. The proportion of carboxyl groups in the sample increases quickly, but the relationship with time is complex, because decarboxylation reactions also occur. Later, Hernadi and Domotor (1981) found that water absorption and wettability decrease with an increase of temperature or duration of thermal treatment.

Beall (1969) used sensitive equipment to measure the weight losses during constant-rate heating of various types of hemicellulose and lignin, both in air and in nitrogen. The weight losses were caused by combustion (oxidation) and pyrolysis. For lignins, the lowest temperature recorded for the start of combustion reactions was 167 C, and for pyrolysis 175 C. For hardwood xylan, the lowest temperature for the start of combustion was 193 C, and for pyrolysis 2 10 C. For softwoods, the most thermally unstable type of hemicellulose was a galactoglucomannan: the lowest starting temperature for combustion was 175 C, and for pyrolysis 180 C. These temperatures indicate that oxidation is a valid concern at the temperatures Chow (1971a) used in studying infrared changes of wood in air.

Auto-crosslinking reactions occur during the heat treatment of hardboard (Back 1987). As a board is heat treated, these reactions can require 1 h at 210 C, but the same reactions occurring just on the surface of a board heated above 100 C should take much less time. Back proposed that the first step of the reactions involves production of radicals and preoxidation of wood polymers. According to Back, carbonyl groups would be formed preferentially in the lignin portion of wood, but some would also form in the cellulosic portion. The second step is crosslinking to form covalent hemiacetal or ether bonds. Acidic conditions catalyze these reactions, and aluminum sulfate is usually added to produce those acidic conditions. Within the fiber, the main effect is decreased swelling and reduced equilibrium moisture content.

Measures for inhibiting oxidation to improve bonding

Aqueous borax solutions of 1% applied to undried wood surfaces were successful in retaining bond quality in the face of high drying temperatures, even in mill trials (Chow 1975). Use of a 2.5% borax solution on veneer surfaces often showed no advantage over a 1% solution. Treatment with 5 and 10% borax solutions usually produced lower bond quality than did treatment with solutions at lower concentrations. For Douglas-fir dried at 180 C, the benefits of borax treatments did not show up until 40 min of drying, a time that is well beyond what veneer would experience even with redrying. However, Douglas-fir contains the extractive dihydroquercitin (Troughton and Chow 1973), a natural antioxidant that comes to the surface during drying. For white spruce dried at 160 C and 180 C, the benefits of 1% borax treatments were evident between 10 and 20 min. Chow

thought the effectiveness of borax might be due to either its bonding with wood hydroxyl groups by chelate reactions or to its inhibition of autoxidation reactions at high temperature. Examples in a U.S. patent (Chow 1979) showed that a 1% borax solution treatment improved the bond quality of plywood made from inactivated veneer. The wood failure values often substantially improved, and the bond strengths usually improved. However, a couple of the examples showed that the borax treatment could not restore all inactivated veneer to the U.S. Product Standard PS 1-83 requirement (APA 1983) of 85% average wood failure. The patent shows that boric acid is generally less effective than borax.

Oxidation used to activate wood for bonding

In contrast to the evidence for negative effects of oxidation on wood bonding with conventional resins, some researchers have used oxidizing agents to activate wood surfaces for bonding. Nitric acid treatment produces additional carboxyl and carbonyl groups on wood surfaces (Collett 1973; Rammon et al. 1982), while hydrogen peroxide treatment produces carboxyl groups, carbonyl groups, and free radicals (Philippou and Zavarin 1984). Nitric acid and hydrogen peroxide have their greatest effects on lignin and comparatively little effect on cellulose (Collett 1973; Rammon et al. 1982; Philippou and Zavarin 1984). Although the initial hope was to bond wood to wood to produce good bonding, it was found necessary to add some additional binding material to the wood particles or flakes. These binders probably act as bridges in the molecular gaps between wood surfaces. Favored binders in the period after the 1970s oil crisis were furfuryl alcohol or lignosulfonates, available from renewable resources. Later, working with phenolic resin adhesive on chemically activated wood particles, Gardner and Elder (1988) found that pine flour treated with 6% to 12% its weight of a 50% aqueous hydrogen peroxide solution lowered the gel time of the resin by 45% to 75% relative to untreated wood. Treatments of pine with 40% nitric acid or 3 N sodium hydroxide also lowered the gel time of phenolic resin, but less so than did the hydrogen peroxide treatment. This indicates that phenolic resin interacts with such activated wood surfaces, although the means of interaction were not shown.

Chemical interference with resin cure

Acidic extractives

Tropical hardwood species. – A few reports have indicated that extractives from some tropical hardwoods impede bonding by interfering with cure of the resin. The best study is probably that of Nguyen (1975). He determined the amounts of water, ethanol, diethyl ether, and benzene extracts of five Southeast Asian hardwood species. Water and ethanol extracts are likely to contain condensed and hydrolyzable tannins and other polyphenolic compounds; the ether extracts are likely to contain fats, resin acids, waxes, and sterols. Water and ethanol extracts were more acidic than ether and benzene extracts. Nguyen determined the effect of ethanol and water extracts on cure behavior of a phenolic resin. The most acidic wood species, kapur and yellow meranti, showed strong buffering action to alkali. The addition of a 10% solution of kapur extractives to the phenolic resin reduced its pH from 11.0 to 10.2. Addition of one part of the alcohol- and water-soluble kapur extracts to nine parts of resin showed that the extracts could reduce

resin gel times from 100 min to near 40 min, thus preventing the resin from flowing properly after that time. This behavior agreed with gel time results on adding hydrochloric acid to the phenolic resin to lower the pH to equivalent levels. The effect on gel time was thus due to acidity, not to reaction of the resin with constituents of the extracts. Ether extractives, which were also quite acidic, accelerated gelation and prevented complete resin cure to a greater extent than did other kapur extractives, but ether extractives were only present at $\frac{1}{9}$ to $\frac{1}{30}$ the amount of ethanol extractives.

Bonding problems are worse for kapur than for the other four species Nguyen studied. The extractives in kapur moved to the surface much more readily than did extractives in the other species. The ease of extractives migration, the low pH level, and the strong alkali-buffering capacity were postulated to cause the significant bonding problems of kapur. However, yellow meranti had higher total extractives content than kapur, and had almost the same acidity and buffering characteristics as kapur. The only major difference I noted was that yellow meranti had lower specific gravity than kapur or keruing (average of 0.45 compared to 0.69 and 0.67, respectively). Interestingly, the species that tended to cause more frequent plywood delaminations were said to be kapur and keruing (Wellons and Krahmer 1973), the denser species. Kapur and keruing showed clean separations (unanchored gluelines) between wood and adhesive, indicated by impressions of wood left in the hardened adhesive. Possible causes given for the clean separations were: (1) the adhesive failed to wet and penetrate the wood, or (2) the adhesive bonded to a thin layer of extractives at the wood surface, or (3) extractives dissolved into the adhesive and accelerated its cure or made it too viscous to penetrate the wood structure.

Jordan and Wellons (1977) concluded that simple wetting measurements on the commercially dried veneers of these tropical hardwood species do not correlate with gluability as determined by percentage of wood failure. They found that commercially dried kapur and light (white and yellow) meranti were quite wettable with pH 11 sodium hydroxide (NaOH) solution, but commercially dried keruing and dark (red) meranti were not very wettable. However, kapur had very low wood failure values despite its good wettability, and dark meranti had high wood failure values despite its poor wettability.

Additional evidence suggests that some wetting phenomenon may be important to bonding kapur and keruing. Sellers (personal communication) found that using phenolic resins with high residual methanol and added wetting agents would allow good bonding to keruing and kapur, indicating that penetration through extractives is important to bonding these species. Burkill (1966) relates that an exudate of freshly cut or tapped Dipterocarpus (keruing) trees is used, along with a bark substance, as a caulk on the inside of boats to protect them from weather. He also notes that a mixture of a camphor (from the kapur tree), castor oil, and resin is used for stopping leaks, presumably for caulking boats.

Oak and pine. – Oak also contains extractives that may interfere with bonding. Roffael and Rauch (1974) found that flakeboards made with chips from old oak had lower internal bond (IB) strengths than did flakeboards made with chips from young oak. Measurements of the pH of boiling-water extracts showed a much lower pH in the old oak than in the young oak, 3.23 compared to 4.23. The difference in pH was maintained even after a second boiling extraction in fresh

boiling water. Aqueous extracts from the young oak showed essentially the same pH values as those observed for pine. However, the alkali buffering capacities in the three trees were different. The pine had comparatively little buffering capacity and responded strongly to the first additions of alkali. The young oak, which had more buffering capacity than the pine, responded more weakly and in a more linear fashion to alkali additions than did the pine. The buffering behavior of the old oak paralleled that of the young oak, but the pH values for the old oak were consistently about 1 pH unit lower than for the young oak. The old oak had over twice the percentage of water-soluble extracts as did the young oak (14% compared to 6.3%, respectively). Extraction of oak chips with boiling water before bonding increased internal bond strength (IB) and bending strength. After two boiling water extractions, oak chips were extracted with boiling 1 N sodium carbonate solution, which is alkaline. After this extraction, the old oak had lost 22.1% of its weight, whereas the young oak had lost only 12.8% of its weight. However, there was little difference in IB strength between boards made with young or old oak chips that had been extracted with sodium carbonate, even for those boards aged in boiling water before they were tested. Internal bond strengths of boards made with flakes extracted with sodium carbonate were much higher than strengths of boards made with unextracted flakes.

Since acidity and buffering capacity of extractives seemed to explain the problem, Roffael and Rauch tried spraying NaOH on unextracted chips before applying the phenolic adhesive. This produced a bondability equal to the best bondability obtained with extracted chips.

Kuo et al. (1 984) studied the effects of drying temperature on bonding properties of white oak and southern red oak. Veneers were dried to an average moisture content of 2%. After drying, substantial deposits were seen in the lumens of fiber tracheids near the veneer surfaces and in the lathe checks, both places where evaporative cooling would take place. In the interior portions of the veneer, the lumen walls were only slightly lined with deposits. Most of these deposits could be removed by extraction with hot water. Surface scrapings from high-temperature dried veneers had abnormally large amounts of water-insoluble extractives. No chemical composition of the water-insoluble extractives was reported. Only wood failure data were reported for the plywood tests. For white oak plywood, the air-dried veneer had the highest wood failure, 20%; veneer that was mill dried to 4% MC or oven-dried at 100 C were grouped next at 16% wood failure; and veneer that was oven-dried at 177 Chad the lowest wood failure at 11%. Red oak plywood made with mill-dried veneer had 24% wood failure, and the other three drying treatments produced wood failures of around 18%. Scraping the surface before bonding had no significant effect on wood failure.

In attempts to improve bonding, several liquids were used to treat the oak veneer surfaces, apparently after drying. The techniques were not described. Water extractions did not produce better wood failure results; rather, this resulted in lower wood failures for boards made with air-dried veneers. Dipping the veneers in 1% NaOH (pH > 13) sometimes raised and sometimes lowered wood failure values. However, soaking the veneers in NaOH solution always helped improve the wood failure. Kuo et al. (1984) mention that the NaOH soak removed two to three times as much extractive material from the surfaces as did the dip treat-

ment. The authors felt these NaOH treatments removed contaminants from the surface and possibly neutralized acidic tannins in the oak. I find it interesting that water extraction did not give the same bond quality improvements as sodium hydroxide treatments, if the problem was water-soluble extractives. However, these results can be reconciled if the cause for poor bonding actually involved the water-insoluble extractives such as fatty aids, which can be de-esterified from the surface and solubilized with NaOH. Sodium stearate is soluble in cold water.

A study on high temperature drying of hardwood flakes used for making flake-board (Plagemann et al. 1984) determined that a relationship exists between board internal bond strengths, total acid content, and dryer temperature. The differences of IB between boards made of the different species were attributed to acid level effects associated with each species (red oak, white oak, and sweetgum). The flakes were air-dried to 30% moisture content before being dried at the test temperatures (20 C, 150 C, and 350 C) down to a uniform 4% MC. Most acid properties (total, soluble, and bound acid contents, and buffering capacity) changed with an inconsistent and weak dependence on dryer temperatures. For the response of flakeboard mechanical properties to Rake drying temperature, statistically significant effects of species were found, but I find nothing more than weak trends among the species. Perhaps no significant indications of inactivation to bonding were seen because no attempt was made to strongly overdry the flakes. A complicating point in this study is that the boards were all pressed to the same density, but the density of the wood species was not examined as a variable in the study. I noted that most of the flakeboard mechanical properties ranked inversely with expected density of the wood species. This trend could be explained by the fact that Rakes of the higher density species would not be forced together as much in producing a set board density as would the lower density species, providing less flake-to-flake contact for the higher density species. Unfortunately, the ranking of acidity in these species is the same as the ranking for the normally expected density; that is, white oak was the most acidic and usually the most dense, and sweetgum was the least acidic and least dense. Therefore, the acidity and the unexamined density factors could have been confused statistically in trying to attribute changes of board mechanical properties to only the acid properties of the wood species. Sellers et al. (1988) noted that high-density species, such as oak, tend to swell and shrink more than less dense species, putting more stress on bonds. He also mentioned that the ring porous anatomy and strong acidity and buffering of oak make it more difficult to bond.

Roffael (1 987) recently examined how drying conditions affect several of the mechanical properties and thickness swell of pine Rakeboards bonded with urea-formaldehyde, phenol-formaldehyde, and isocyanate resins. The flakes were all reequilibrated to between 9 and 12% MC before hot pressing, unlike the industrial practice of using flakes nearer 3 to 7% MC. The worst changes in bonding occurred in isocyanate boards, where the IB strengths decreased as the flake drying process became increasingly severe. It is not clear to me that the smaller changes observed in other properties, or for the other resins, are statistically or physically significant. Roffael found that the acidity and, especially, the buffering capacity of the Rakes increased as more acetic and formic acids were generated within the wood by more severe drying.

Other extractives

Plomley et al. (1976) found that a chestnut tannin extract and some Eucalyptus hydrolyzable tannin extracts, as well as quercitin and ellagic acid, can cause low-quality phenolic bonds when present on wood surfaces at quantities of 2 g/m^2, especially when the bonds are tested wet. Plomley reasons that these tannin substances can produce lower bond strengths by either reacting with resin molecules or masking the surface, thereby preventing the resin from bonding to wood in the normal manner.

CONCLUDING REMARKS

This review has evaluated research literature on ways in which excessive drying may inactivate wood to bonding. The review concentrates mostly on bonding by hot-press, alkaline phenolic adhesives. The evidence has been organized under two main categories: physical responses and chemical reactions to excessive drying. The physical responses reviewed in Part I (Christiansen 1990) include exudation of extractives to the surface, which lowers wettability or hides the surface; reorientation of wood surface molecules, which reduces wettability or eliminates sites for bonding; and irreversible closure of large micropores in cell walls, which inhibits wetting and decreases the number of internal anchoring points. In Part II, chemical reactions involved in mechanisms for inactivation include degradation of wood surface strength, oxidation and pyrolysis of surface bonding sites; chemical interference with resin cure or bonding; and elimination of surface hydroxyl bonding sites by ether formation.

Wellons (1 977) commented that all of the mechanisms initially proposed for surface inactivation appear valid to some degree, with oxidation of surfaces possibly the most important. I agree that many of the mechanisms are operative in different situations, but would emphasize that the loss of wettability by extractives is the mechanism most likely to be encountered in plywood production utilizing Douglas-fir or southern pines, which are both particularly susceptible to inactivation.

Many things are happening simultaneously during high-temperature drying of wood. The critical point is to isolate which reactions are leading to the particular problem under investigation.

The species effect and even the effect of the within-tree origin of veneer (Hancock 1964) on the susceptibility of Douglas-fir to inactivation indicate the importance that extractives must have on inactivation. I am not convinced that fatty acids are effective catalysts for oxidation, as Chow suggested (1971a). It seems more likely that migration of fatty acids, or some extractive component, is the major factor causing inactivation in selected species.

The oxidation and pyrolysis mechanisms for inactivation are real and inevitable at high enough temperatures and long times. My interpretation of the data is that oxidation is a relatively slow process at the temperatures where inactivation is usually encountered in drying pines, Douglas-fir, and larch (and perhaps some other coniferous species), and therefore oxidation is not an explanation for surface inactivation in these cases. Where fatty acid concentrations are relatively low or perhaps where the wood is uniformly porous, the effects of fatty acids may be minimized and oxidation is the operative mechanism for inactivation. I feel that

if other mechanisms involving the effects of extractives on wettability, acidity, or access to surfaces do not cause inactivation in the moderately high-temperature range, then oxidation, pyrolysis, molecular reorientation, and/or cell wall closure mechanisms will of necessity occur at the higher temperatures and longer times and eventually lead to surface inactivation of wood to bonding.

Some of the inactivation mechanisms reviewed, especially those involving the acidity of extractives, are likely to produce different results when acidified urea-formaldehyde adhesives or near-neutral resorcinol-formaldehyde adhesives are used.

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