MICROSCOPY OF ACID-ACTIVATED BONDING IN WOOD[1]

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ABSTRACT

Fluorescence and scanning electron microscopy were used to reveal the effect of nitric acid on activated bonding in wood. The physical properties of the treated wood were analyzed and the feasibility of the bonding technique was evaluated. Results showed that the technique was too severe as it greatly damaged the wood. On both sides of the bond line the cells were crushed beyond identity. Below this zone was a zone of darkened wood, 20 to 50 cells, that was undistorted or partially distorted. Fractured surfaces in samples with high shear strength showed conventional wood failure, while low shear strength samples exhibited amorphous masses of destroyed wood and partially distorted cells. Longitudinal views of fractured surfaces indicated that the acid diffuses readily through cell walls, cell lumina, and intercellular spaces. Lignin and lignin-containing gap fillers applied during acid treatment did not seem to change the action of the acid on the wood. Addition of filter paper and walnut shell flour gap fillers caused deeper penetration of the acid into the wood.

Keywords: Microscopy, cell structure, fractured surfaces, fillers, maple, birch, Douglas-fir.

INTRODUCTION

The worldwide shortage of energy and increasing cost of synthetic adhesives have stimulated adhesive researchers to find new and less expensive chemicals for bonding structural wood products. One class of inexpensive and readily available chemicals is acids, which are thought to promote bonding by chemically activating the wood surfaces. Bonding is believed to occur by chemical transformation of cell-wall constituents, carbohydrates, and lignin into compounds that bond auto-adhesively. Researchers have shown that acid-bonded wood products have mechanical properties comparable to those of phenolic-resin bonded wood (Johns et al. 1978).

At the Forest Products Laboratory, experiments have been carried out with several acids and oxidants (Kelley 1981; Rammon 1981; Young et al. 1982; Rammon et al. in press). This report covers microscopic examination of wood samples treated with nitric acid. The purpose of this research was to examine how acid affects the physical properties of wood, to evaluate the feasibility of this bonding technique, and to discover some information on the bonding mechanism itself.

MATERIALS AND METHODS

Blocks of 5/16-inch-thick (7.9 mm) lumber, 5 inches (127 mm) wide, and 7¼ inches (184 mm) along the grain, were sprayed over one surface with 40% nitric acid at a level of 0.5 pound per square foot (2.4 kg/m^2). After a specified open

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assembly time, the treated surfaces of two blocks of the same species were placed in contact with each other and the panel bonded by hot pressing for 1 h at 212 F (100 C) and at 300 psi (2.07 MPa) for hardwoods and 200 psi (1.38 MPa) for softwoods. Bonded panels were prepared from hard maple, yellow birch, and Douglas-fir. In some cases gap-filling materials were incorporated in the bond line during the acid treatment stage. The material was applied to one of the surfaces to be bonded after approximately half the acid had been sprayed on the wood surface. The remaining half of the acid was then sprayed onto the gap-filling material. The gap-filling materials were selected to represent certain lignin-cellulose combinations.

The bonded panels were cut into shear test specimens, 1 inch (25.4 mm) wide with a 1-inch (25.4 mm) overlap. After being tested for shear strength in the dry condition on a universal testing machine, the broken specimens were examined microscopically on both the fractured surface and along transverse sections.

For fluorescence microscopy (FM) of transverse sections, wood block surfaces of about 1 square centimeter were smoothed by freezing microtomy and examined in a reflected, near-ultraviolet light (peak transmission at 365 nm). For scanning electron microscopy (SEM), the surfaces were coated with gold in a sputter coater and observed with a Cambridge Stereoscan, Type 2A.

RESULTS AND DISCUSSION

All samples—maple, yellow birch, and Douglas-fir—became very brittle after nitric acid treatment, which imparted a reddish-brown color. Fluorescence microscopy of transversely sectioned fracture surfaces showed that the effects of acid treatment followed by pressing were similar for all samples evaluated. On both sides of the bonding line, a wide zone of massively crushed wood was revealed in which individual cells were unrecognizable (Fig. 1). Thus the depth of this zone could not be expressed in terms of a number of cells but in the units of linear dimensions, which ranged from 160 to 1,000 microns. In this dark zone the rays were also crushed and showed a wavy appearance; cracks extending parallel to the fracture surfaces or the rays were common. The dark zone of totally crushed wood was followed by a darkened area of wood in which the cells were undistorted or partially distorted. The depth of this zone varied between 20 to 50 cells.

One sample had a high shear test value evidenced by the fracture line (at top of Fig. 1) passing through the wood unaffected by acid. In another sample the fracture line passed through the bonding zone (Fig. 2). Corresponding surface views of these samples are shown in Figs. 3 and 4. Figure 3 reveals a conventional wood failure both transwall and intrawall with cross strips and serrate features, which imparted roughness to the exposed surface. Figure 4 shows amorphous masses of degraded tracheids and partially degraded tracheids that were separated mainly at the middle lamella. Generally, cells that are still recognizable show that separation during the shear test has taken place at the middle lamella or the primary wall. This suggests that lignin has been affected by the nitric acid more intensively than the carbohydrates, since the capacity of lignin to bind with the adjacent cell-wall layers appears to be lowered. These results are consistent with previous studies (Rammon 1981; Rammon et al. 1982) indicating that lignin is more readily attacked by nitric acid.

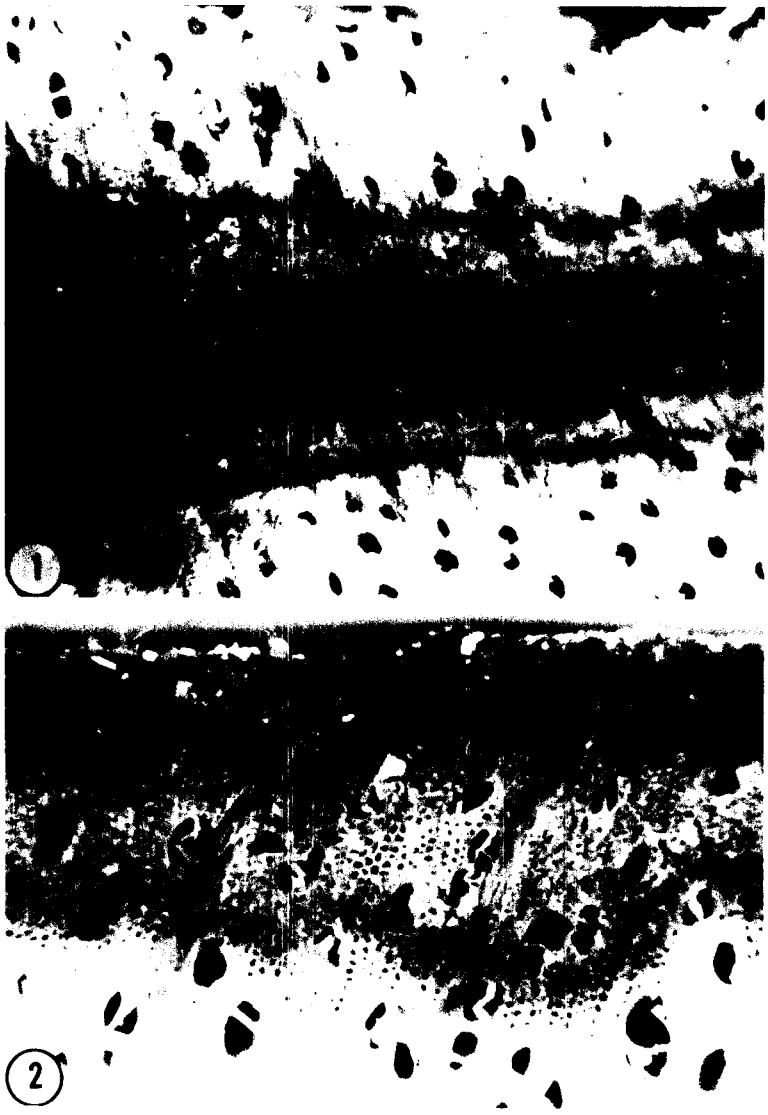

FIG. 1. Transverse section of fractured maple with failure line passing through the acid-unaffected wood (FM). 75×.

FIG. 2. Transverse section of fractured maple with failure line passing through the bonding zone (FM). 120×.

The effect of nitric acid on yellow birch samples did not appear to be markedly different from that on hard maple. Birch also showed a layer of totally degraded wood beneath the bonding surface. However, the depth of degradation was usually slightly greater than that in the maple. Below the degraded wood was a layer of darkened wood with uncrushed or partially crushed cells. Similarly, scanning electron microscopy surface views of fractured surfaces also showed failure in which the fracture line had passed through the middle lamella or the primary wall, or it showed clumps of severely degraded cell-wall material.

FIG. 3. Surface view of fractured surface in maple showing transwall and intrawall failure with cross strips and serrate features (SEM). 1,000×.

FIG. 4. Surface view of fractured surface in maple showing amorphous masses of damaged cells and partially damaged cells exposing middle lamella (SEM). 1,000×.

In Douglas-fir the dark zone of totally crushed cells extended more deeply into the earlywood than into the latewood (Fig. 5). Hence the weaker earlywood was crushed more severely than the less affected latewood and gave rise to a "ridging" effect. When the panels were subjected to pressure bonding, the bonding surface consisted of high-pressure contact points formed in the latewood and low-pressure contact points in large areas of the earlywood. This may be one reason why Douglas-fir samples had low shear strength values and often delaminated (Ram-

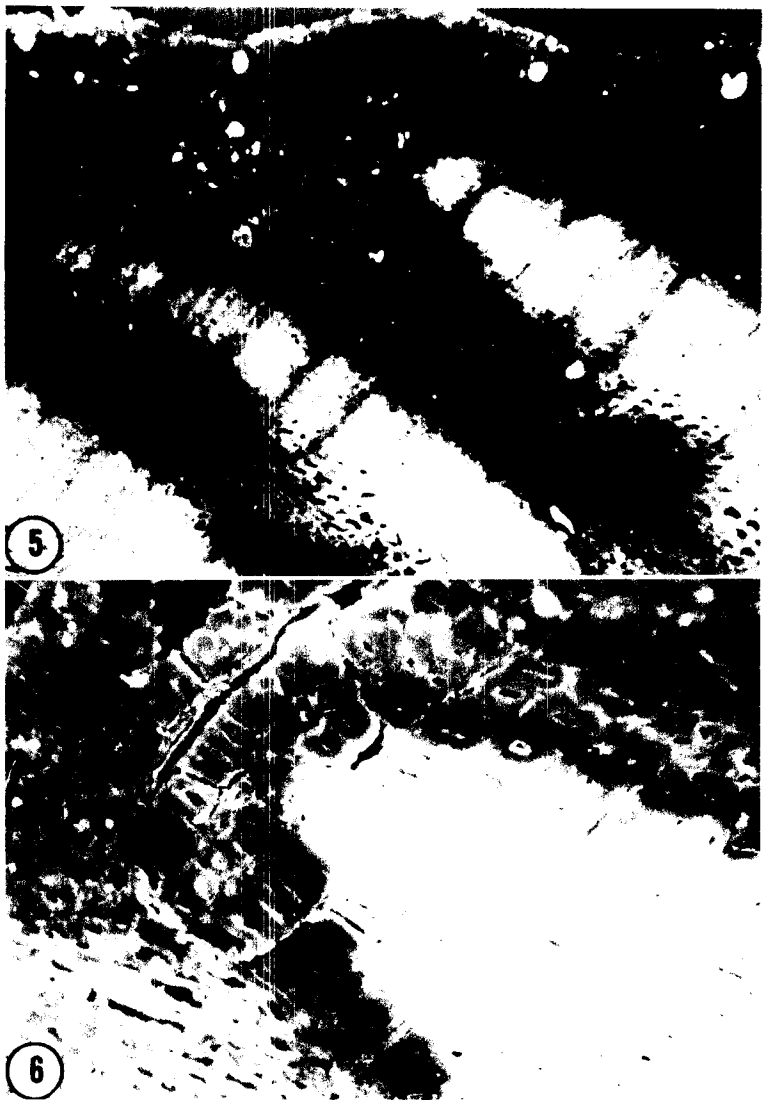

FIG. 5. Transverse section of fractured Douglas-fir showing deeper penetration of acid into earlywood than latewood (FM). 90×.

FIG. 6. Transverse section of fractured Douglas-fir showing cracks in latewood that separate tracheids at the middle lamella and also extend along the rays; earlywood is severely crushed (FM). 250×.

mon et al. in press). The differential crushing occurred even though the Douglas-fir samples were subjected to a lower bonding pressure (200 psi instead of 300 psi) than was used for the hardwoods. Higher magnification photomicrographs of Douglas-fir samples showed cracks that were more frequent in latewood than in earlywood (Fig. 6). The cracks separated tracheids at the middle lamella and extended along the rays. Fractured surfaces showed severely degraded tracheids as clumps of amorphous, modified wood substance (Fig. 7).

Longitudinal views of the fractured surfaces suggest that the acid action pro-

FIG. 7. Surface view of fractured surface in Douglas-fir showing amorphous clumps of damaged tracheids (SEM). 1,000×.

FIG. 8. Longitudinal view of fractured maple showing acid proceeding through cell walls, cell lumina, and intercellular spaces (FM). 120×.

ceeded equally well whether the cells have or do not have their lumina in contact with the bonding line; that is, the action proceeded through the cell walls, the cell lumina, and the intercellular spaces as if wood were a structural complex of homogeneous nature (Fig. 8). Therefore the orientation of growth increments with respect to the bonding line seemed to be immaterial.

In samples with lignin or lignin-containing (kraft paper) gap fillers, the action of the acid is not different from that on wood without the fillers (Fig. 9). Fractured surfaces of those samples showed characteristics of the gap filler (kraft paper fibers), the underlying wood (Fig. 10), and maple lignin arranged in clumps of irregular

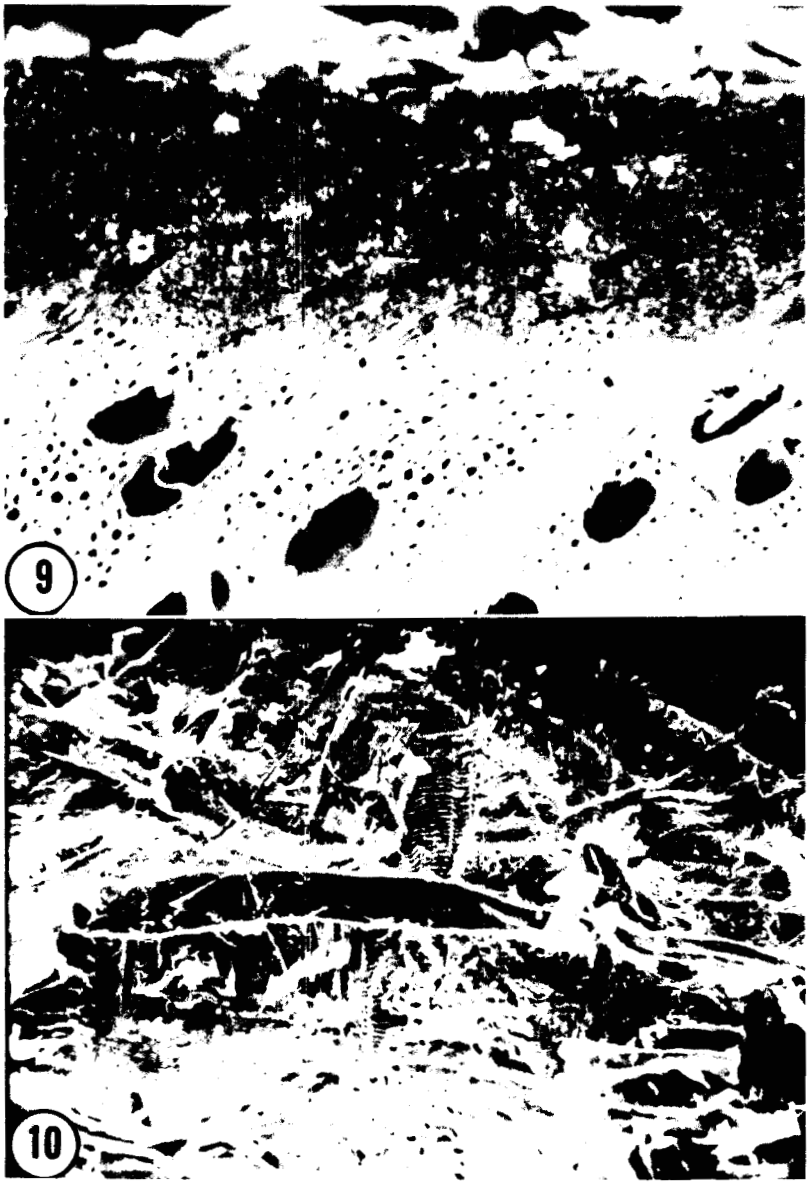

FIG. 9. Transverse section of fractured maple with maple kraft paper gap filler (FM). 150 ×.
FIG. 10. Surface view of fractured surface in maple with kraft paper gap filler (SEM). 200 ×.

size and shape (Fig. 11). In a fluorescence photomicrograph of a sample with maple lignin as a gap filler (Fig. 12), the wood (bright) and lignin (dark) can be distinguished by their color differences.

With filter paper and walnut shell flour gap fillers, the action of acid on wood appeared to be greatly enhanced—the wood is affected to a two to three times greater depth than with the gap fillers consisting either partially or entirely of lignin. These results indicated that lignin reacted with the nitric acid at the surface

FIG. 11. Surface view of fractured surface in maple with maple lignin gap filler showing lignin clumps of irregular size and shape (SEM). 1,000×.

FIG. 12. Surface view of fractured surface in maple with maple lignin gap filler showing wood (bright) and lignin (dark) (FM). 150×.

more intensively than did the carbohydrates, and this slowed the penetration of acid into the wood.

CONCLUSIONS

Microscopic results indicated that the nitric acid bonding procedure used on wood samples caused extensive destruction of the cells. A chemical alteration of the cell-wall constituents must have taken place because the cell walls have under-

gone large changes in their physical properties. The separation of cells at the middle lamella or primary wall suggested that lignin was preferentially attacked. Orientation of growth increments with respect to the bond line did not show much influence on action of acid since the acid affected wood as if it were a structural complex of homogeneous nature. There were some differences between softwoods and hardwoods in response to the acid. In Douglas-fir, due to the different action of acid on the latewood and earlywood, a "ridging" effect resulted that caused poor bonding. Unfortunately, no judgments could be made on the nature of the bonding mechanism itself.

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