NOTES AND CORRESPONDENCE

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No discussion will be published unless the author of the original article has been provided with a copy of the discussion and has had an opportunity to submit a reply to the Editor, to be published with the discussion. Discussions and replies should not exceed the length suggested above. Where pertinent, references to the literature should be included.

It is anticipated that discussion and replies in *Wood and Fiber* can add, for both authors and readers, a dimension not normally found in technical journals.

Studies of Penetration of Phenol-Formaldehyde Resin into Wood Cell Walls with the SEM and Energy-Dispersive X-ray Analyzer[1]

PREFACE

The following technical note is offered as an extension of and a rebuttal to the article by Bernard M. Collett in the Summer 1970 issue of *Wood and Fiber*, **2**(2): 113–133. We were impressed by the historical review and technical coverage given to SEM by Mr. Collett. However, we felt that readers of *Wood and Fiber* would be left with an erroneous, or at least incomplete, impression of the analytical capabilities of this instrument. Admittedly, accessories are required to accomplish what is described in the following preliminary note. Nevertheless, we were of the opinion that some indication of this type of instrumentation potential should have been made in the article. Actually, his diagram in Fig. 3 included X-ray detection, but no mention of its use was made. In fact, the emphasis on the secondary electron detection mode when used for studies of the interface between wood substrate and adhesive or coating was perhaps too great.

The primary advantages of the SEM over the TEM are the greater depth of field and easier specimen preparation. However, even the SEM does not differentiate well between unpenetrated wood cell wall and wood cell wall that has been penetrated with resinous material. Hence, neither the TEM nor the SEM permits observation and photographic recording showing the extent of resin penetration into the wood cell wall without tagging the resin in some manner.

If the SEM is operated in conjunction with an energy-dispersive X-ray analyzer, its usefulness as a research tool is markedly extended by yielding semi-quantitative as well as qualitative information. Now heterogeneous systems can be analyzed on the micro level with a minimum of specimen preparation. In addition, this instrumentation is particularly useful for biological material since the normal elements comprising this material are not detected by the analyzer, thereby simplifying the identification of any tagging element from sodium through uranium.

The wood-adhesive interface system can

[1] The cooperation and advice of Mr. Gary Cogswell, Dr. John Russ, and Mr. A. Kabaya of the JEOLCO (U.S.A.) Applications Laboratory, Medford, Massachusetts, are gratefully acknowledged.

be analyzed on the micro level within cell walls without the necessity of "seeing" the resin within the cell wall. Preliminary results of such a study on Douglas-fir and Southern yellow pine bonded with a phenol-formaldehyde resin at 300 F under 200 psi for 12 min show a concentration gradient of resin across the cell wall at the wood-adhesive interface. Maximum concentration of resin occurs in the secondary wall close to the lumen filled with adhesive. Significantly lesser amounts of resin were found at each point of analysis across the cell wall, with no resin found in the middle lamella. Springwood cell walls were penetrated to a greater extent than summerwood cell walls. The maximum concentration of resin observed in any cell wall was less than 10%.

Veneer of the two species, ⅛ inch thick, was bonded with a brominated phenol-formaldehyde resin. The resin was purified so that only bromine, the tagging element, was chemically attached to the resin molecules. Random areas of the glue line were selected for embedding in methyl methacrylate. Approximately ¼-μm sections, showing wood in cross section plus the glue line, were made with an ultramicrotome and mounted on filmed EM specimen grids.

With the SEM set in the transmission mode, a P/N Polaroid picture was taken to aid in the selection and to provide a permanent record of the points (approximately ¼ to 1 μm in diameter) for analysis. Although the sections are nonconducting, there was no build-up of static charge, thus eliminating the need for metalizing the specimen surface. Counting time for each analysis ranged from 400 to 1,800 sec at 20 keV. During the analysis, checks were made periodically to be sure that the electron beam had not drifted. A digital printout of the 400-channel analyzer provided a record of the elemental analysis.

In previous studies (see REFERENCES), it had been found that small molecular weight molecules or ions could be responsible for the optical evidence of penetration of materials into wood cell walls. For example, sodium hydroxide in phenol-formaldehyde adhesive causes the wood cell walls to fluoresce at the same color as does the phenol-formaldehyde, thereby presenting the problem of differential absorption of only the sodium hydroxide by the cell walls. Similarly, certain solvents in coatings produced the same change in color of the wood cell walls when observed with the fluorescence microscope as produced by the coatings themselves.

In a study of adhesive-bonded wood products by Collett, lead oxide was dissolved in sodium hydroxide in the adhesive, or powdered lead oxide was added directly to the adhesive to improve the contrast between the wood and adhesive in the SEM. Lead ions are significantly smaller than intermediate molecular weight phenol-formaldehyde molecules, thereby posing the problem of differential absorption. A second problem, recognized by Collett, was that some of the patterns of contrast in the SEM alone could result from redistribution of the adhesive during the preparation of the sections.

It is believed that the present technique also overcomes this limitation because of the cross-linked nature of the phenol-formaldehyde resin, the chemical attachment of the tagging element to these molecules, and the fact that no adhesive was found in certain areas of the cell wall.

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