

IMPREGNATION OF WOOD WITH A HIGH VISCOSITY EPOXY RESIN

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ABSTRACT

A method is described for impregnating small wood specimens with a high viscosity epoxy resin, without the use of a diluent to reduce viscosity. The method relies upon the strong temperature-dependence of viscosity, in conjunction with a curing agent that does not polymerize rapidly at high temperatures. Some preliminary results for a variety of Northeastern species are presented.

Keywords: Epoxy, impregnation.

INTRODUCTION

The use of epoxy systems as impregnants for wood has received only limited attention in the past few years, despite their excellent physical, chemical, mechanical, and shrinkage characteristics. This limitation is due in large part to their viscous nature. In the few instances where they have been utilized (Blankenhorn et al. 1977; Bartolomucci 1979), it has been in conjunction with reactive or inert diluents, which substantially lower the viscosity and permit easier impregnation.

From an analytical viewpoint, it is desirable to utilize epoxy resins (particularly the predominant diglycidyl ether of bisphenol A varieties) without the complication of a diluent. The effects of diluents are not well known in systems as complex as wood, and their presence complicates any analyses. A method is described here for impregnating small wood specimens with high viscosity diglycidyl ether of bisphenol A-based epoxies without the use of a diluent. This method relies primarily upon the strong temperature-dependence of viscosity, in conjunction with a curing agent that does not polymerize rapidly at high temperatures. A preliminary evaluation of the techniques is also presented using a wide range of Northeastern species.

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TABLE 1. *Characteristics of the components of the impregnant.*

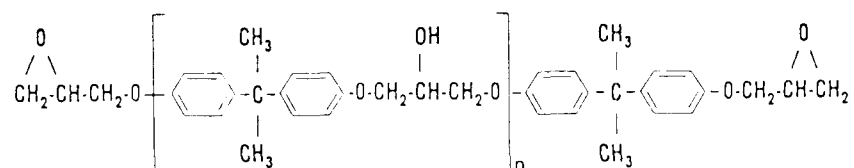
Component	Form	Properties
Epoxy resin	Liquid	Molecular weight = 370–385 g/mol Viscosity at 20 C 20,000 centipoise 75 C 100 centipoise Functionality = 2 Flammability hazard: Flash point = 480 C (open cup); but when heated to decomposition, it emits highly toxic fumes Health hazard: Low toxicity via oral route
Curing agent (meta-phenylenediamine)	Solid	Molecular weight = 108 g/mol Melt temperature = 63 C Functionality = 4 Flammability hazard: Slight; but when heated to decomposition, it emits toxic fumes Health hazard: Highly toxic via oral, subcutaneous, and intravenous routes. Being tested for carcinogenic effects

References: Sax 1979; NFPA 1978; Borgstedt and Hine 1973.

DESCRIPTION OF THE PROCEDURE

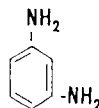
Preparation of the impregnant

The impregnant is a stoichiometric mixture of Epon 828* and meta-phenylenediamine (mPDA). Some pertinent characteristics of each of these materials are summarized in Table 1. The epoxy resin (Epon 828) is based upon diglycidyl ether of bisphenol A, and has the following structure:



It is a polydisperse material whose weight is reported to be 370 to 385 grams/mole, which corresponds to average values of n between 0.08 and 0.6, respectively. At room temperature, the viscosity of this material is approximately 20,000 centipoise, but this can be reduced to a more acceptable 100 centipoise, by heating to approximately 70 C (Anonymous 1967). The resin should be maintained at this temperature in a bath prior to mixing with the curing agent.

The meta-phenylenediamine curing agent has the following structure:



* Epon 828 is a Shell Chemical Co. product.

Unlike the resin, it is a solid at room temperature, and has a melt temperature of 63 C. It should be melted in a separate container in the bath prior to mixing with the epoxy resin. It is necessary to melt this material first, since it will not dissolve completely if it is added directly to the resin. Presumably, this is due to a layer of epoxy polymerizing on the surface of the curing agent before it can dissolve completely. A slight amount of stirring is required to mix the molten mPDA with the epoxy resin, but this stirring will not cause the formation of many air bubbles because of the low viscosity of the solution. After mixing, the system will increase in viscosity as it cools, but it will not harden appreciably for several hours. Reducing the amount of curing agent relative to the amount of resin will increase the pot life, but with the sacrifice of strength in the final product.

Impregnation process

A vacuum-pressure-soak procedure has been found to be the most effective method for intensive impregnation of wood specimens with the system just described. The samples should be oven-dried prior to placing them in the impregnation chamber. As the vacuum (200 microns or 2.7×10^{-3} kPa is sufficient) is being developed over the samples, the impregnant can be prepared. It should be backfilled into the chamber as soon as the components are mixed, since if it remains at 70 C in the bath for an appreciable amount of time, a noticeable increase in viscosity will occur because of premature polymerization.

After sufficient impregnant enters the chamber and covers the samples, the remaining vacuum should be released and an overpressure applied using nitrogen gas (200 psig or 1,379 kPa). The samples can be allowed to soak for up to 2 hours at this pressure if the system is not thermally insulated. The pressure should then be slowly released over a period of 20 to 25 minutes.

When the samples are removed from the chamber, they should be wiped free of excess resin and allowed to "first-stage" cure for 24 hours at 21 C. Following this, they should be further cured, using elevated temperature. In our studies, we have found that 24 hours at 52 C, followed by 24 hours at 105 C, gives satisfactory results. This three-step process was found appropriate for obtaining good castings of solid, defect-free epoxy control specimens, and it does not necessarily represent the optimum curing conditions for impregnated wood samples. Further details concerning the nature of the impregnant and the impregnation procedure are given elsewhere (Moore 1981).

PRELIMINARY EVALUATION OF TECHNIQUES

Sample preparation

For preliminary evaluation of this process, a number of small samples representing a variety of Northeastern species were obtained. These samples were taken from 14 trees harvested in Centre and Huntingdon counties in Pennsylvania during the winter of 1979. The species represented by these trees are summarized in Table 2. The logs were livesawn, and selected boards were dried in two mixed loads using standard kiln drying procedures (Rasmussen 1961). Three end-matched cylindrical specimens (0.95 cm in diameter and 1.59 cm in length) were machined from one board representative of each species. These were oven-dried, weighed, and then impregnated, using a different cycle time for each of the three cylinders

TABLE 2. Species examined in a preliminary evaluation of the impregnation technique.

Common name	Scientific name
1. Black cherry	<i>Prunus serotina</i> Ehrh.
2. Black locust	<i>Robinia pseudoacacia</i> L.
3. Black walnut	<i>Juglans nigra</i> L.
4. Eastern hemlock	<i>Tsuga canadensis</i> (L.) Carr.
5. Red elm	<i>Ulmus rubra</i> Muhl.
6. Red maple	<i>Acer rubrum</i> L.
7. Red oak	<i>Quercus rubra</i> L.
8. Red pine	<i>Pinus resinosa</i> Ait.
9. Sweet birch	<i>Betula lenta</i> L.
10. White ash	<i>Fraxinus americana</i> L.
11. White oak	<i>Quercus alba</i> L.
12. White pine	<i>Pinus strobus</i> L.
13. Willow	<i>Salix</i> sp. L.
14. Yellow-poplar	<i>Liriodendron tulipifera</i> L.

within a group. The three cycles differed only in length of time at 200 psig (1,379 kPa), and are illustrated in Fig. 1.

Results and discussion

The amount of impregnant retained by a given wood sample can be expressed in several ways. One of the most convenient methods is as a volume fraction; that is, the fraction of the total composite volume occupied by the impregnant. In nonswelling systems (such as the one in the present study), volume fraction

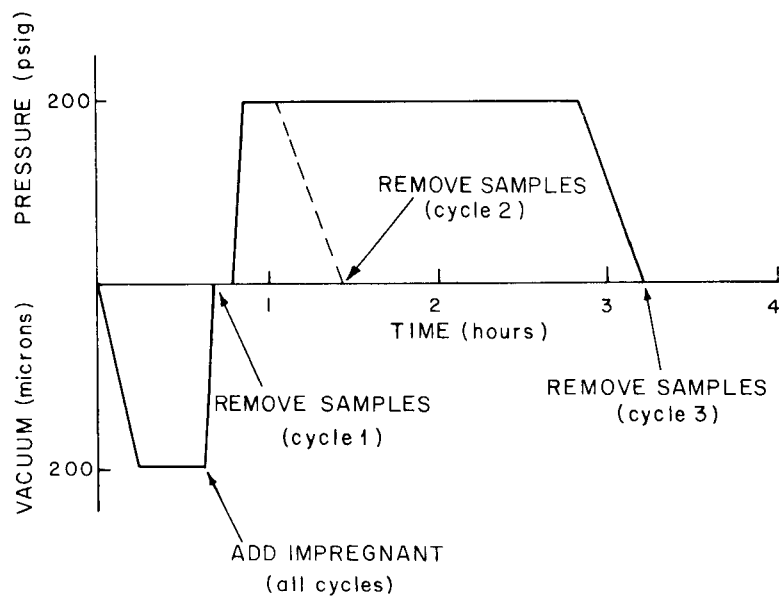


FIG. 1. Impregnation cycles used in study.

TABLE 3. Volume fraction of impregnant obtained for various species in a preliminary evaluation of the procedure.

Species	Oven-dry density [*] (grams/cm ³)	Volume fraction of impregnant ^{**}		
		Cycle 1	Cycle 2	Cycle 3
White pine (heartwood)	0.383	0.305	0.475	0.530
Black locust (heartwood)	0.693	0.021	0.032	0.044
Eastern hemlock (heartwood)	0.442	0.349	0.517	0.548
Willow (sapwood)	0.472	0.423	0.573	0.641
Willow (heartwood)	0.565	0.241	0.509	0.545
Yellow-poplar (sapwood)	0.393	0.589	0.702	0.683
Yellow-poplar (heartwood)	0.461	0.128	0.574	0.612
White oak (sapwood)	0.634	0.168	0.400	0.433
White oak (heartwood)	0.724	0.051	0.154	0.226
Red maple (sapwood)	0.598	0.321	0.490	0.541
Red pine (sapwood)	0.396	0.452	0.698	0.688
Red pine (heartwood)	0.498	0.061	0.096	0.156
Black cherry (heartwood)	0.617	0.203	0.320	0.360
Red elm (heartwood)	0.774	0.194	0.267	0.305
White ash (sapwood)	0.742	0.170	0.290	0.381
Sweet birch (sapwood)	0.747	0.247	0.455	0.451
Black walnut (heartwood)	0.599	0.181	0.369	0.457
Red oak (heartwood)	0.676	0.146	0.185	0.230

* Average of three end-matched samples.

** Each value corresponds to one of three end-matched samples for a given species.

of impregnant can be determined by the following expression (Moore 1981; Siau 1971):

$$v_m = \left(\frac{m_e}{m_w} - 1 \right) \left(\frac{\rho_w}{\rho_m} \right) \quad (1)$$

where:

v_m = volume fraction of impregnant

m_e = oven-dry mass of the impregnated material

m_w = oven-dry mass of the wood prior to impregnation

ρ_w = density of the wood prior to impregnation (based on oven-dry mass and volume)

ρ_m = density of the impregnant

Table 3 summarizes the volume fractions of impregnant obtained from the heartwood and sapwood specimens examined. As might be expected from such a diverse group of species, a wide range of impregnant volume fractions was observed. The data for the various cycle times suggest, however, that for many species, most of the uptake occurred during the first few minutes of the cycle. This is reasonable since the specimens were relatively small, and the viscosity of the impregnant was lowest during the initial stages of the cycle.

When comparing the impregnability of a variety of species having different densities, it is frequently useful to eliminate the density variable. This can be accomplished by expressing the retention of impregnant in terms of the fraction

TABLE 4. *Fraction of voids filled for the longest impregnation time.*

<i>Highest fraction of voids filled ($F_v \geq 0.8$)</i>
Willow sapwood (0.94)
Red pine sapwood (0.93)
Yellow-poplar sapwood (0.92)
Red maple sapwood (0.90)
Sweet birch sapwood (0.90)
Yellow-poplar heartwood (0.88)
Willow heartwood (0.87)
<i>Intermediate fraction of voids filled ($0.5 < F_v < 0.8$)</i>
Eastern hemlock heartwood (0.78)
Black walnut heartwood (0.76)
White ash sapwood (0.75)
White oak sapwood (0.75)
White pine heartwood (0.68)
Red elm heartwood (0.63)
Black cherry heartwood (0.61)
<i>Lowest fraction of voids filled ($F_v \leq 0.5$)</i>
White oak heartwood (0.44)
Red oak heartwood (0.42)
Red pine heartwood (0.23)
Black locust heartwood (0.08)

of voids that are filled by the polymer (F_v). F_v is the ratio of the impregnant volume fraction (v_m) to the void volume fraction of the unimpregnated wood (v_v). Equation 1 is used to calculate v_m , while v_v is calculated using the following expression (Siau 1971):

$$v_v = 1 - \frac{\rho_w}{\rho_{ws}} \quad (2)$$

where:

v_v = void volume fraction of the unimpregnated wood

ρ_w = density of the unimpregnated wood (based on oven-dry mass and volume)

ρ_{ws} = density of wood substance (1.5 g/cm³)

Table 4 classifies the species examined in the present preliminary survey into three groups, on the basis of fraction of voids filled by the polymeric impregnant. The cut-off values used to define the three classes are somewhat arbitrary, but similar to those used by others (Siau et al. 1978) for a methyl methacrylate-based impregnant.

It is evident from Table 4 that the proportion of voids filled varies greatly among the species and heartwood/sapwood combinations examined. Those with the lowest fraction of voids filled include: red pine heartwood, black locust heartwood, red oak heartwood, and white oak heartwood. Low retention has been observed in several of these species by other investigators using other impregnants (Siau et al. 1978; Young and Meyer 1968), and the physical and anatomical reasons for

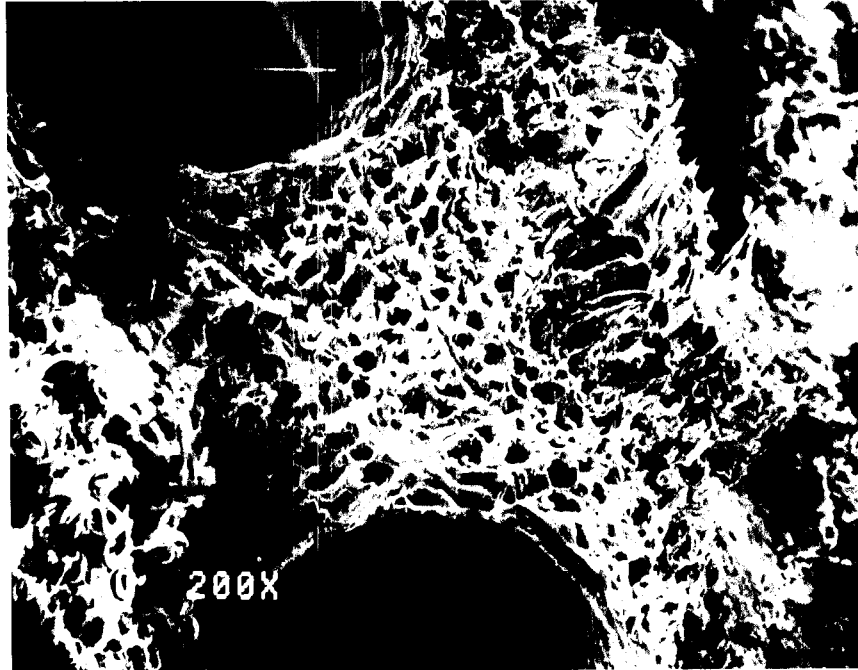


FIG. 2. SEM micrograph of unimpregnated red oak heartwood.



FIG. 3. SEM micrograph of impregnated red oak heartwood.

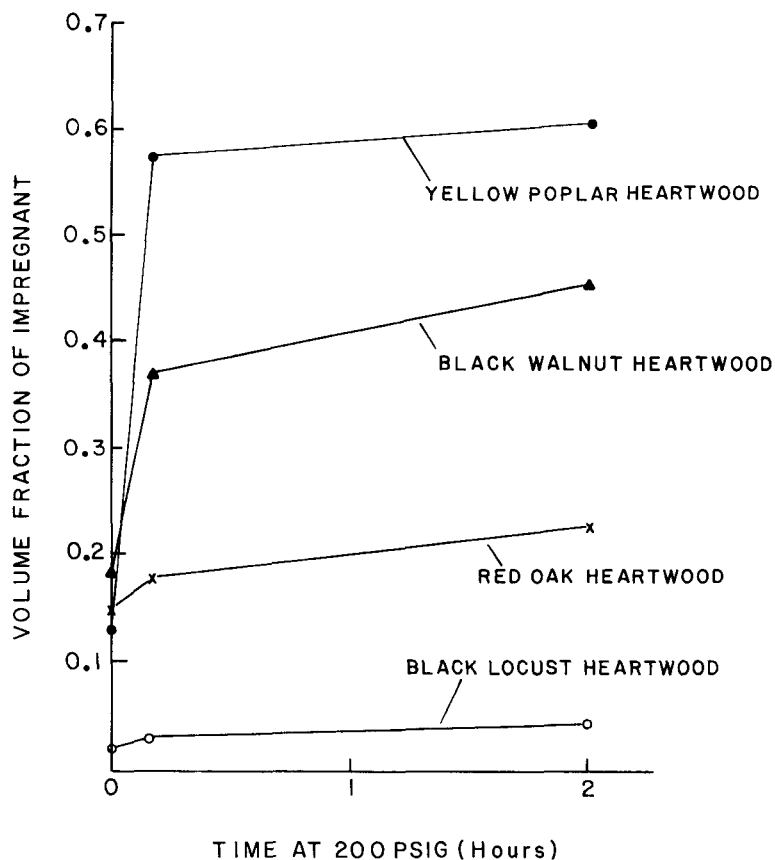


FIG. 4. Rate of uptake of impregnant for red oak and other species during the impregnation process.

this are discussed in the literature. The low retention in white oak heartwood, for example, is generally attributed to the tyloses, which occlude the vessel elements. The red pine heartwood specimens and the black locust heartwood specimens exhibited only surface retention of impregnant, while the red and white oak heartwood specimens retained some impregnant within their interiors. The red oak heartwood specimens responded much differently from the white oak specimens, however. In this case, the low volume fraction of impregnant was apparently not due to low permeability (as in the white oak case), but rather to a large inaccessible volume. During the impregnation process, the large vessel elements of the red oak specimens filled rapidly with impregnant, while other portions of the structure did not. Figures 2 and 3 illustrate the selectivity of the impregnant. The high permeability of the vessel elements is reflected by the significant volume fraction of impregnant that was achieved early in the cycle, but that did not increase much with time compared with that for other species. This is shown in Fig. 4, in which volume fraction of impregnant is plotted against time at 200 psig (1,379 kPa) during the cycle. The values at zero time are those obtained using cycle 1 (see Fig. 1).

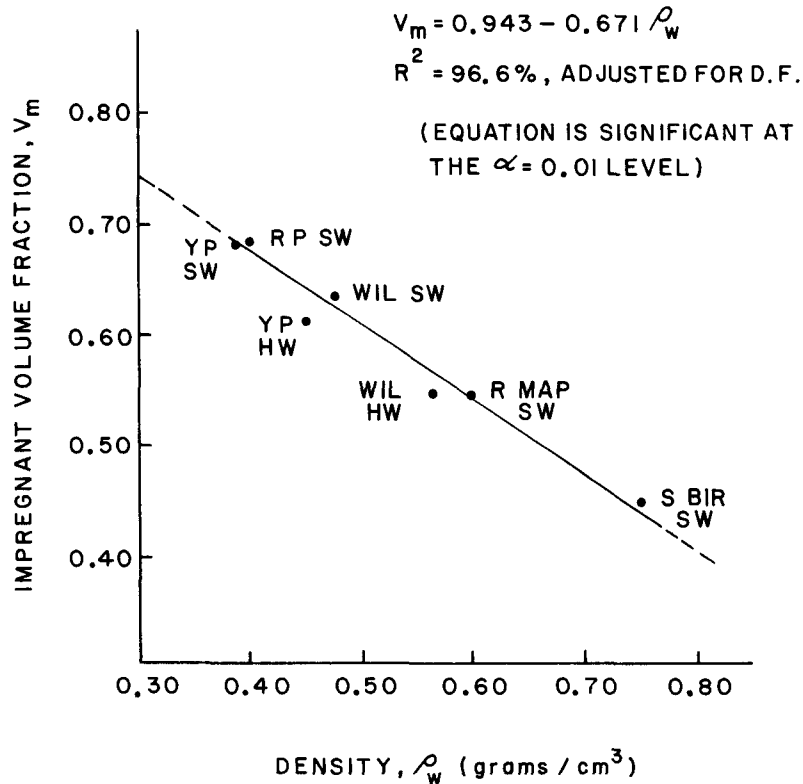


FIG. 5. Relationship between substrate density and impregnant volume fraction for selected species.

All other species and heartwood/sapwood combinations investigated showed higher retention of impregnant. Those with the highest fraction of voids filled include: red pine sapwood, yellow-poplar sapwood and heartwood, willow sapwood and heartwood, red maple sapwood, and sweet birch sapwood. Within this group, there is a strong correlation between oven-dry density and volume fraction of impregnant, as illustrated in Fig. 5. In these species some cellular selectivity apparently also exists. For example, Figs. 6 and 7 are SEM micrographs of yellow-poplar sapwood before and after impregnation. In this case, the vessel elements again appear receptive to the impregnant, while thicker walled fibrous elements do not.

It is interesting to compare these results with previously published data for similar species impregnated with methyl methacrylate-based systems. While there are significant differences in the natures of epoxies and methyl methacrylate, some common ground appears to exist in wood impregnated with these two materials. The results in the present study for red pine, black cherry, and red maple, for example, are in good qualitative agreement with the data of Young and Meyer (1968) for the same species impregnated with methyl methacrylate. Young and Meyer (1968) found, for example, that retention of impregnant in red pine was

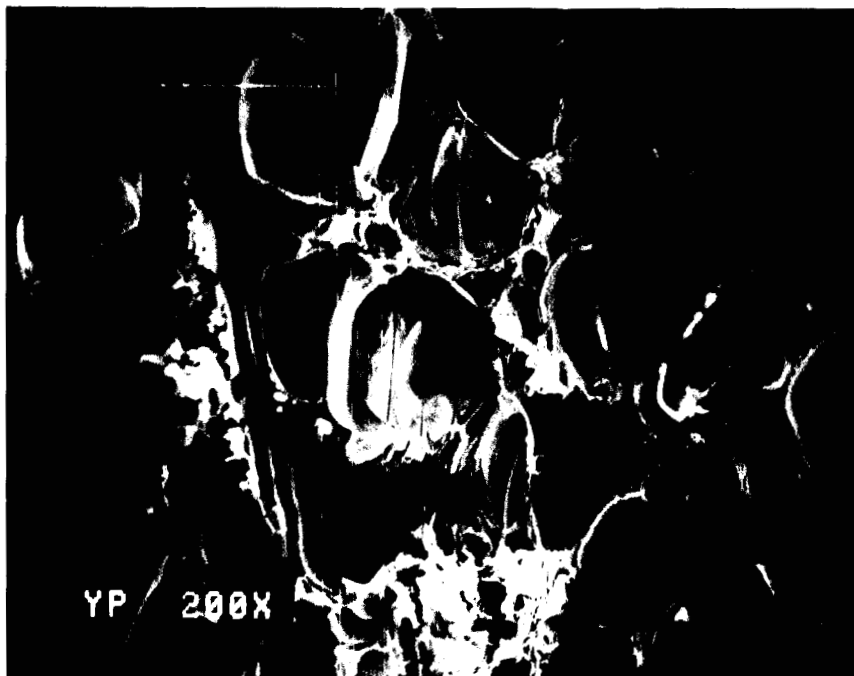


FIG. 6. SEM micrograph of unimpregnated yellow-poplar sapwood.

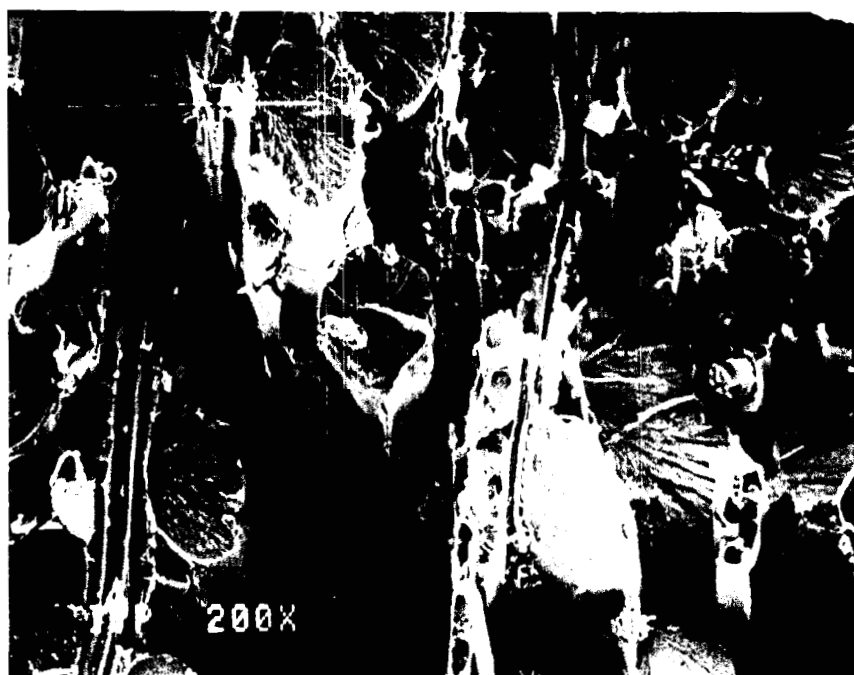


FIG. 7. SEM micrograph of impregnated yellow-poplar sapwood.

relatively low for the heartwood ($v_m^* = 0.04$), and relatively high for the sapwood ($v_m^* = 0.44$). Additionally, black cherry heartwood was found to have a relatively low retention of impregnant ($v_m^* = 0.29$) compared to red maple sapwood ($v_m^* = 0.42$) having a similar density. Siau *et al.* (1978) reported on the impregnability of a variety of southern hardwoods using a crosslinkable acrylic system. They classified the species they examined as easy, moderate, and hard to treat, depending upon the fraction of voids that were filled by the monomer. They also found that yellow-poplar and red maple were relatively easy to impregnate, while many white oak and red oak species were rather difficult. These similarities suggest that the permeability and accessibility restrictions that apply to the acrylic impregnants also apply to the epoxy system used in the present study.

There are some fundamental differences between epoxy and acrylic impregnants that affect quantitative comparisons of retention values. The volumetric shrinkage that occurs during the polymerization of methyl methacrylate is on the order of 21%. This implies that 21% of the void volume accessible to the monomer will not contain polymer in the finished product. Other effects, such as evaporation during polymerization, can increase this value to approximately 29% (Siau *et al.* 1978). Epoxy resins, on the other hand, have low vapor pressures and exhibit relatively low shrinkage during polymerization. The shrinkage of the stoichiometric Epon 828/meta-phenylenediamine system used in the present study is reported to be approximately 6% (Anonymous 1967). This relatively low value is supported by Figs. 3 and 7, and explains why higher polymeric impregnant volume fractions are possible with epoxy systems than with methyl methacrylate-based impregnants.

SUMMARY

A method has been described and preliminary results have been presented for the impregnation of small wood specimens with a high viscosity diglycidyl ether of bisphenol A-based epoxy resin without the use of a diluent. The method described was used to impregnate a wide variety of Northeastern species. Interpretation and discussion of the data were made on the basis of volume fraction of retained impregnant, relative to the original density of the substrate. The process was found suitable for many of the species examined. In at least two of the species, the impregnant was strongly selective in terms of the cellular elements that were entered. SEM micrographs of impregnated red oak and yellow-poplar showed that the vessel elements in these species filled rapidly with the impregnant, while the fibrous elements did not. Results dealing with the effects of epoxy impregnation on the physical properties of various substrates are being prepared for future publication.

REFERENCES

- ANONYMOUS. 1967. Epon resins for casting. Shell Chemical Co., Plastics and Resins Division, New York.
- BARTOLOMUCCI, J. R. 1979. Flexural properties and dimensional stability of continuous two-phase bark-polymer composites. M.S. thesis, The Pennsylvania State University.

* Calculated using Eq. 1 and assuming no swelling.

- BLANKENHORN, P. R., W. K. MURPHEY, L. R. RISHEL, AND D. E. KLINE. 1977. Some mechanical properties of impregnated bark board. *For. Prod. J.* 27(6):31-38.
- BORGSTEDT, H. H., AND C. H. HINE. 1973. Toxicity, hazards, and safe handling. *In* C. A. May and Y. Tanaka, eds. *Epoxy resins chemistry and technology*. Dekker, New York, NY.
- MOORE, G. R. 1981. Dynamic mechanical properties of some wood-polymer composite materials. Ph.D. thesis, The Pennsylvania State University.
- NATIONAL FIRE PROTECTION ASSOCIATION. 1978. *Fire protection guide on hazardous materials*. 7th ed. Boston, MA.
- RASMUSSEN, E. F. 1961. *Dry kiln operator's manual*. U.S.D.A., Agric. Handbook No. 188 USGPO, Washington, DC.
- SAX, I. B. 1979. *Dangerous properties of industrial materials*, 5th ed. Van Nostrand Reinhold Co., New York, NY.
- SIAU, J. F. 1971. *Flow in wood*. Syracuse University Press, Syracuse, NY.
- , W. B. SMITH, AND J. A. MEYER. 1978. Wood-polymer composites from southern hardwoods. *Wood Sci.* 10(3):158-175.
- YOUNG, R. A., AND J. A. MEYER. 1968. Heartwood and sapwood impregnations with vinyl monomers. *For. Prod. J.* 18(4):66-68.