DISTRIBUTION OF PHENOL-FORMALDEHYDE RESIN IN IMPREGNATED SOUTHERN PINE AND EFFECTS ON STABILIZATION[1]

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Abstract. Two low-molecular-weight phenol-formaldehyde (PF) resins impregnated at 20% resin-solid concentration in southern pine (SP) wood and cured at 180°C for 20 min were studied by various microscopic methods. The micrographs indicated that the ray tracheids of SP were the main flow path of resin, rays were reinforced by cured resin, and flow of resin into lumens was more difficult for higher-molecular-weight resin. Some PF resin deposits were found in lumens. PF resin deposits were formed to connect ray tracheids and longitudinal tracheids, resulting in interlocking bridges that possibly reduced dimensional changes of wood in the tangential direction. These resin deposits appear to be responsible for the high dimensional stability observed in this direction. The diffusion of PF resins into cell walls appears to occur through rays or primary walls, but not through lumens or the warty layer.

Keywords: Phenol-formaldehyde resin, resin flow path, wood impregnation, wood dimensional stability, wood microscopy, resin distribution.

INTRODUCTION

Low-molecular weight (MW) phenol-formaldehyde (PF) resins have been used as impregnants for dimensional stabilization of wood at relatively high resin-solid concentration levels of 25% or more (Forest Products Laboratory 1999). For commodity-type wood composite products such as oriented strandboard (OSB), such high resin-solid concentration levels would be too expensive. In an earlier paper (Wan and Kim 2006), several low-MW PF resins were impregnated in southern pine (SP) wood specimens at low concentration levels using a vacuum and pressure method, and the wood samples were hot-pressed in the radial direction. Similarly, PF resins were impregnated into 60:40 SP-wood and mixed-hardwood strands using the same methods at low resin-solid concentration levels of 1–2%, and made into strandboard to see if the approach could be useful for dimensional stabilization of OSB. The study showed that the impregnated PF resins improved certain strength properties of strandboard as well as the thickness swell performances of compressed SP wood and strandboard. The reasons behind these results were explored by various microscopic methods.

Various instrumental methods have been used to study impregnated chemicals in wood structures: light microscopy (Morita and Sakata 1991;

Kamke et al 1996; Xu et al 1999), scanning electron microscopy (SEM) (Postek et al 1980; Wang et al 1992; de Silveira et al 1995; Song and Hwang 1997; Rozman et al 1998), transmission electron microscopy (TEM) (Nearn 1974; Parameswaran and Himmelreich 1979; Murmanis et al 1986; Singh and Dawson 1996; Petric et al 2000), confocal microscopy (Matsumura et al 1998), and energy dispersive spectroscopy (EDS) (Vigdorovich and Chalykh 1984; Bolton et al 1988; de Silveira et al 1995). Microscopic methods generally lack quantitative measures and reproducibility, and the sample preparation procedures often cause artifacts and misleading observations. However, they offer a direct observation of impregnated chemicals or resins in wood structures to indicate the impregnation flow path and resin distribution, and often provide clues to the interaction between wood structure and resins. Therefore, in this study, SP wood specimens impregnated with two different low-MW PF resins at 20% solids concentration were cured and investigated by using various microscopic methods to help better understand the reasons behind the improved wood stabilization by low dosage of low-MW PF resins.

MATERIALS AND METHODS

Materials, resin impregnation procedures, and other handling procedures of specimens in this study were described earlier (Wan and Kim 2006). Briefly, resins PF1 (MW 310) and PF3 (MW 451) were synthesized in the laboratory and used for impregnation of SP wood specimens. Wood specimens were $40 \times 19 \times 5$ mm (longitudinal x tangential x radial) in dimensions and equilibrated to 10% moisture content. Impregnation of resins was carried out in a cylinder by applying a vacuum (-98 kPa) for 15 min and then air pressure (690–828 kPa) for 30 min. The resin-impregnated wood samples were cured at 180°C for 20 min without compression.

Light microscopy, SEM, TEM, EDS, and confocal microscopy were used. Sample preparation procedures were described elsewhere (Wan 2000). Briefly, for light microscopy, the resin-impregnated SP wood specimen was sliced in the radial direction with a sliding-knife microtome in the thickness range of 20–40 µm and then stained with safranin and mounted on glass slides. Specimens for SEM observation were dried at 105°C for 24 h and then coated with gold and palladium. Samples for TEM were subjected to a series of procedures of fixation, rinsing, osmication, dehydration, infiltration, and embedding, and then cut with a diamond knife for observation. The sample preparation method for confocal microscopy was the same as that for light microscopy but without staining, since PF resins in wood specimens fluoresce differently from wood (Kuo et al 1994). The sample preparation method for EDS was similar to that of SEM except that the coating was carried out with carbon instead of gold and palladium. The light microscopy was done with an Olympus Vanox research microscope; SEM with a Cambridge S-360 scanning electron microscope; TEM with a JEOL 100-CXII transmission electron microscope; confocal microscopy with a Leica TCSNT confocal laser scanning microscope; and EDS with a Cambridge S-360 scanning electron microscope having a Tracor Northern TN-2000 energy dispersive spectrometer.

RESULTS AND DISCUSSION

Flow path of PF resins impregnated in SP wood

The confocal micrograph of a cross-section of an SP specimen impregnated with resin PF1 (Fig 1), digitally modified for black-and-white reproduction, shows dark-colored resin deposits, indicating that the flow path of resin was mainly through the rays. The light micrograph of a wood specimen impregnated with resin PF3 shows resin deposits (Fig 2), revealing that the resin flowed mainly through the ray tracheids. The confocal micrograph (Fig 3) shows more clearly that the flow path of resin is the ray tracheids and not ray parenchyma, since resin deposits are present in ray tracheids but not in ray parenchyma adjacent to the resin-clogged ray tracheids. The confocal micrograph of den-
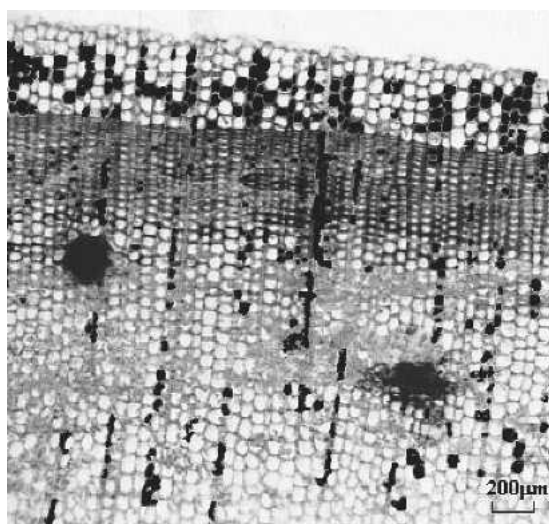
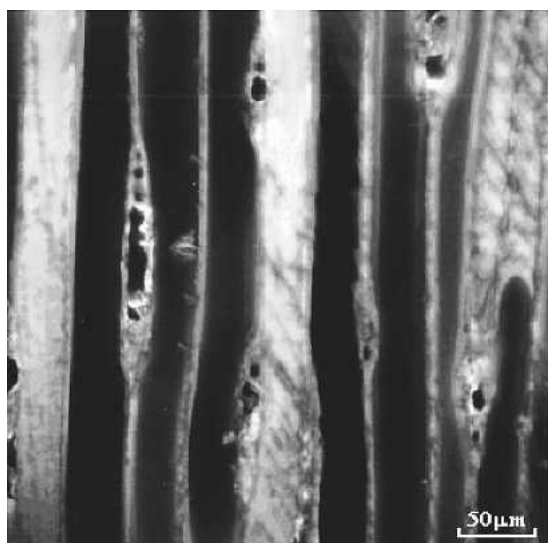FIGURE 1. PF resins in the cross-section of an SP strand by confocal microscopy.

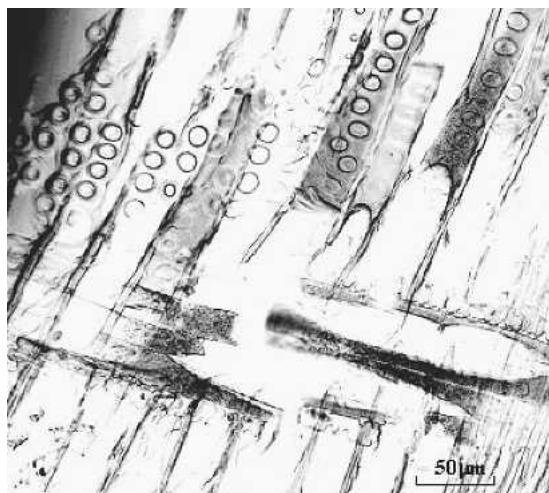FIGURE 3. PF resins in ray tracheids and lumens by confocal microscopy.

FIGURE 2. PF resins in the radial face of a SP strand by light microscopy.
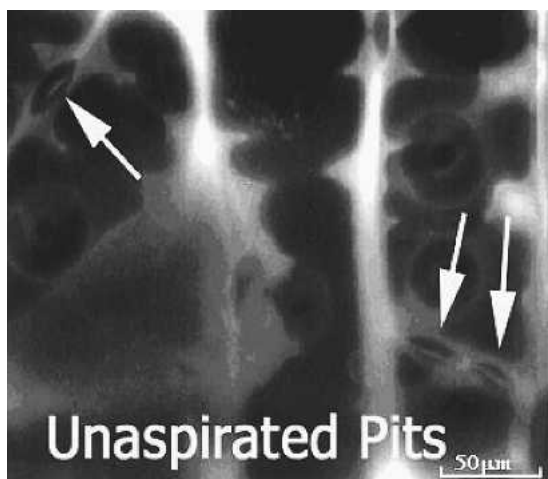

Unaspirated Pits

FIGURE 4. Dentate ray tracheid of a SP strand by confocal microscopy.

tate ray tracheids of untreated SP wood specimens shows that all tori of pit-pairs are unaspirated (Fig 4), which agrees with the results of Nicholas and Siau (1973), who reported that pits in the ray tracheids of SP are usually unaspirated to permit only the chemicals of smaller sizes to pass through them. The micrographs of Figs 2 and 3 also confirmed that the half-bordered pit membranes between ray tracheid and parenchyma have a lower permeability for PF resins (Nicholas 1999).

The observation of resin deposits in wood cell lumens in micrographs of Figs 1 and 2 is contrary to previous research results in that PF resins were claimed to deposit almost entirely on wood cell walls when the resin solids concentration level was below 30% (Stamm and Seborg
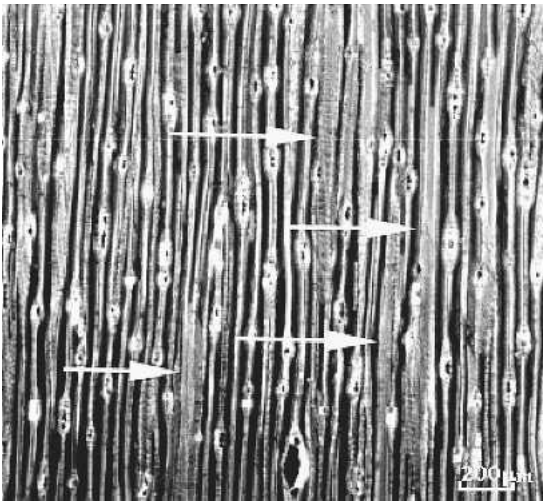
FIGURE 5.   PF resin #1 in the tangential face of a SP strand by confocal microscopy (arrows point to resin—smooth gray areas in photo).

1939). The confocal micrograph of the end-matched, earlywood tangential section of wood impregnated with resin PF1 (Fig 5) shows that the resin has flowed through the ray tracheid pits and deposited in the lumens of longitudinal tracheids. On the other hand, the confocal micrograph for resin PF3 (Fig 6) showed that most resin deposits were locked within the ray tra-
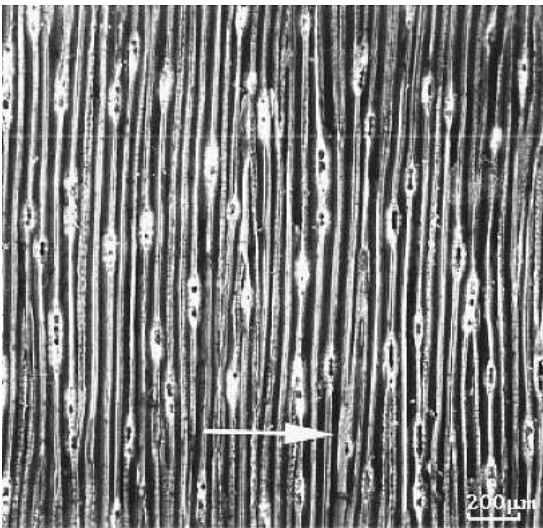

FIGURE 6.   PF resin #3 in the tangential face of a SP strand by confocal microscopy (arrow points to resin).

cheids by ray tracheid pits, with little resin deposit in the lumens of longitudinal tracheids due to the higher MW resin. The filtering action of tori and margos of ray tracheid pits by PF resin molecular sizes appears to be able to permit a more effective, low-level resin impregnation method by choosing the appropriate resin MW.

Dispersion of resins through middle lamella

Would it be possible for resin to migrate through the cell wall by diffusing through the warty layer or the S_3 layer? In the TEM micrograph of Fig 7, between the dark resin deposits in the pit chamber or lumen (A) and those in the cell wall (B), there is nothing but the cell wall. This result indicates that resins do not flow through the warty layer but through the middle lamella, indicating higher permeability of the latter. This micrograph also shows that after impregnation of resin and curing, the resin in the cell wall polymerizes differently from the resin in the pit chamber or lumen as indicated by the resin deposit size difference. Lumen cell walls conduct water, and warty layers do not permit water to diffuse through the cell wall. Cellulose in wood is packed most densely in the area near the lumen and somewhat loosely in the primary wall (Kelsey 1963). Since the molecular sizes of PF resin are larger than water, PF resins would have difficulty in diffusing through cell walls. The main function of rays is to store fat, protein, sugar, etc, and to transport these relatively large molecules to the nearby cells for growth (Met-
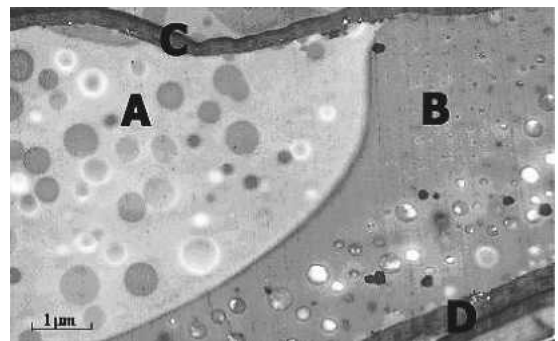

FIGURE 7.   PF resins in cell wall by TEM.

calfe and Chalk 1979). The MW of the PF resin (310–451) is similar to that of fats so the rays may permit resin molecules to flow into nearby cells.

Interlocks formed by impregnated resins

The resin deposits in the lumen and pit-pairs (Fig 8) in the latewood cross-section indicate that the resin flowed through two pit-pairs into lumens, resulting in formation of interlocks between two longitudinal tracheids. Since most pits in SP wood are located on the radial face and pit canals are oriented tangentially, the resin interlocks were formed in the tangential direction. In an earlier report (Wan and Kim 2006), SP wood specimens impregnated with PF resins at 1–5% resin solids concentration levels and cured under compression showed a high anti-swelling efficiency (ASE), especially in the tangential direction. The interlocking resin deposits observed appear to be responsible for the high ASE by restraining wood cell movements. The lighter-colored section in the interlock appears to indicate a break that probably occurred during the sample preparation.
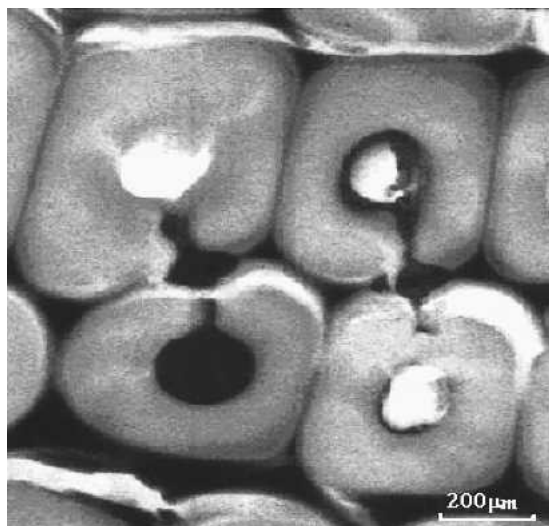
Reinforcement of rays by impregnated resins

The light micrograph of Fig 2 shows dark-colored resin deposits (PF3) in ray tracheids. The confocal micrograph of Fig 9 shows how the resin (PF3) deposited in a ray tracheid. The pit at the upper left of the ray tracheid may be aspirated with the resin at the top of the pit. On the ray tracheid in the lower right, there is an unaspirated pit. Some resins appear to have penetrated into the cell through the margo of the pit. These facts indicate that the resin deposits hardened or reinforced the ray structure. According to the ray restraint theory (Panshin and Zeeuw 1980), rays stiffened or reinforced by impregnated resins will restrain dimensional changes of the wood in the radial direction, improving the overall dimensional stability of wood.

Overall, impregnated PF resins appear to be able to effect ray reinforcement for reduced dimensional changes in the radial direction, form interlocks for lower dimensional changes in the tangential direction, and bulk lumens for reduced wood cell shrinkage. Based on the ASE performance observed (Wan and Kim 2006), the interlocking mode would be more desirable since it would require the least amount of resin for wood dimensional stabilization. The inter-

FIGURE 8. PF resin in latewood pit and lumens by confocal microscopy (darker areas are resin).
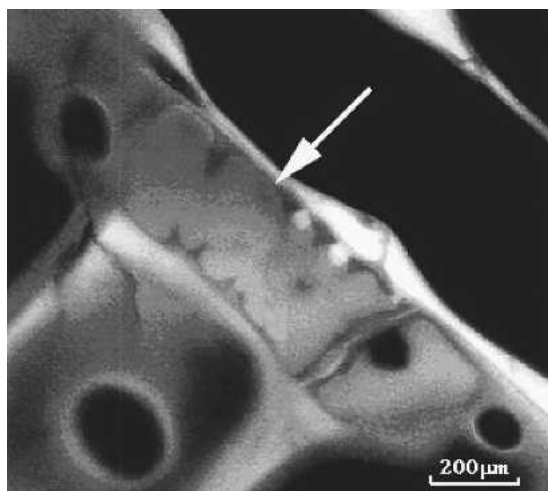

FIGURE 9. PF resins and pits by confocal microscopy (arrow points to resin).
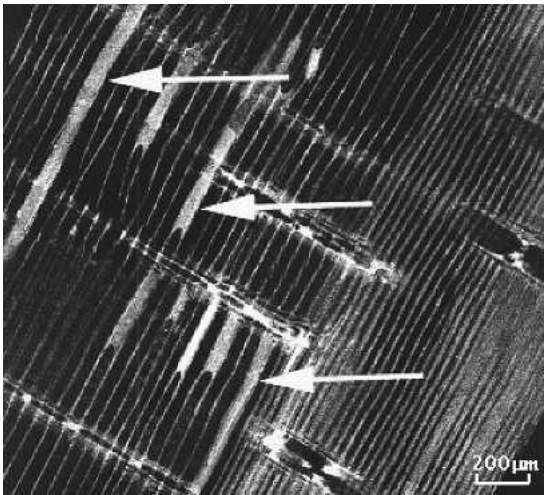
FIGURE 10.   PF resins in earlywood and latewood lumens by confocal microscopy (arrows point to resin).

FIGURE 11.   PF resin in lumen by SEM.

FIGURE 12.   PF resins and cell wall by SEM.

locking concept would be worthwhile to investigate further for wood dimensional stabilization at low resin loading levels.

Variation of resin distribution

At the right side pit-pair in the confocal micrograph of Fig 8, the resin deposits formed almost two rings in two lumens. At the left side pit-pair, one lumen has no resin deposits while the other is full of resin. This observation indicates that there could be a large variation in the resin distribution when resins are impregnated at 20% resin solids concentration. The confocal micrograph of Fig 10 shows PF resins are irregularly located in tracheid lumens in the earlywood and latewood sections. More resins are deposited in the earlywood lumen than in the latewood lumen as shown by arrows. The SEM micrograph of Fig 11 shows resins (PF3) deposited in the lumen tightly bonded with cell walls, but the SEM micrograph of Fig 12 shows a gap between cell wall and resin deposits, possibly from resin shrinkage in curing and/or from damage during sample preparation. These photos show that resin distribution in SP wood, in most cases, varies greatly.

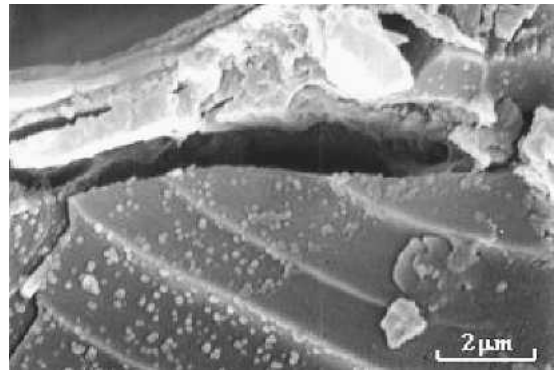## Optimal resin distribution mode for minimal resin concentration level

At 20% PF resin concentration, the resin deposited in lumens will bulk only a few tracheid lumens as in Fig 2. Since the size of tracheid lumens is much greater than that of ray tracheids (Fig 9), the lumens take up large amounts of resin that bulk but contribute little to dimensional stabilization. If one could selectively reinforce ray tracheids of wood by PF resin impregnation as observed in this study and limit the movement of materials into adjacent tracheid lumens by resin interlocks, the dimensional stability of the ray tracheid related wood cells and longitudinal tracheids, the dimensional stability of the wood specimen in tangential direction should be improved. In other words, the ideal resin deposition would be in the ray tracheids, or ray tracheids and pits.

The total volume of rays in SP wood is about 7.6% (Panshin and Zeeuw 1980), and that of ray tracheids is about 2% if it is assumed to be one-fourth of the ray volume (Conners 2000; Panshin and Zeeuw 1980). Based on the observation of Fig 3, one can see that the assumption is quite reasonable. If all of impregnated resin can be deposited in the ray tracheids, the necessary resin concentration level would be about 2% of wood volume, which might be able to interlock all pit-pairs and restrain dimensional changes in tangential direction. Using higher levels of resins than that needed for filling ray tracheids may have little additional bulking effect, which may explain why a PF resin concentration level increase of five times did not increase the dimensional stability or average ASE by that order (Wan and Kim 2006).

Technically, assuming that the flow path of resin in SP is ray tracheids, it is also possible to use only about 2% of wood volume. As discussed above (Figs 5 and 6), controlling the MW of impregnating resins appears to be able to provide a way of controlling penetration, although the optimized MW or size needs to be more clearly defined in a further research.

Optimal resin impregnation procedure

Once the resin flows into ray tracheids, further vacuum or pressure treatments may push the resin into lumens, lowering the resin concentration in ray tracheids and the reinforcements. This scenario may explain the fact that, after a vacuum treatment, further pressure treatment on PF-resin impregnated SP strands shows a lower dimensional stability of SP strandboard (Wan and Kim 2006). On the other hand, treating SP specimens with PF resins by the common spraying method will not force resins to penetrate into the ray tracheids. PF resins applied by spraying on wood strands and storing them for 24 h at room temperature for possible diffusion of resins to occur did not reduce the thickness swelling of strandboards (Wan and Kim 2006) compared with that of strandboard made of vacuum-treated strands. These results suggested that there would

be an optimal impregnation procedure for dimensional stabilization of strandboards.

Nature of cured PF resins

The confocal micrograph of Fig 13 shows resin deposits (PF1) in a lumen obtained by transmitted light. The TEM micrograph of Fig 7 shows a cross-section of a pit chamber with resins. In these micrographs, cured resins show as black spots. A SEM micrograph of a fractured surface of cured resin PF1 of Fig 14 observed without any coating showed white dots, which were found to be sodium chloride (NaCl) crystals by EDS, formed from sodium hydroxide of resin and chloride ions present in water. The formation of sodium chloride indicates that part of the sodium hydroxide resin-curing catalyst is neutralized during curing, and this phenomenon would be more pronounced when resins are cured in contact with wood since certain acid species of wood would become available. This would lead to a different (slower) curing mode for resins in contact with wood from the bulk of resin, an inhomogeneous resin curing as suggested in literature (Detlefsen 1999). The black spots are perhaps the cured PF resin clusters that
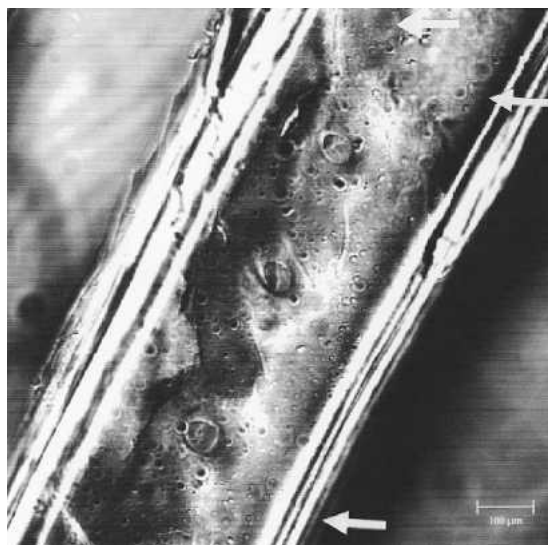

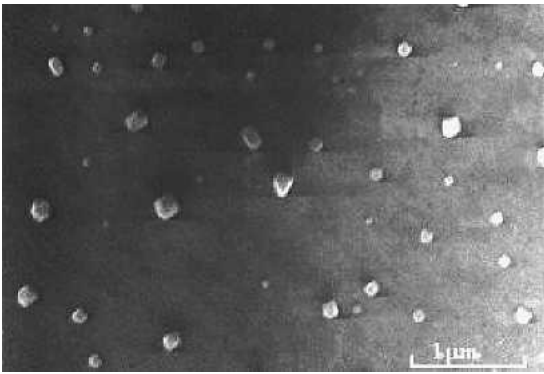FIGURE 13.   PF resins in lumen by confocal microscopy.

FIGURE 14. Uncoated PF resin system by SEM.

have a higher density than other areas. Further research would be useful.

CONCLUSIONS

SP specimens impregnated with two MW PF resins at 20% levels and cured at 180°C for 20 min were studied by various microscopic methods for resin distributions. The study indicated that the ray tracheids would be the main flow path of PF resins; rays are reinforced by impregnated PF resins; and the flow of PF resins into lumens were inhibited for higher MW or larger molecules. Some resins were deposited in the lumen that may have only a bulking effect. The PF-resin deposits that connect ray tracheids and longitudinal tracheids may have formed interlocks between cells resulting in smaller dimensional changes of SP wood specimens in the tangential direction. The results indicate that the low resin-solids concentrations used in the earlier study would be cost-effective in treatments of SP for improvement of dimensional stability. The diffusion of PF resins into cell walls appears to occur through rays or primary cell walls, but not through lumens or warty layers. PF resins impregnated into wood may have three functions: ray reinforcing, interlocking, and bulking. Interlocking may be the most effective way to improve SP strand dimensional stability, which in turn improves the dimensional stability of strandboards. This study suggested that dimensional stabilization of strands or strandboard by resin impregnation is related to wood structure, resin MW, and the impregnation process.

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