A Scanning Electron Microscopic Study on the Morphology of Beech Wood (*Fagus crenata*) Copolymerized with Acrolein Using the Xanthate Method of Grafting

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Synopsis

Powdered beech wood (*Fagus crenata*) copolymerized with acrolein by using the xanthate method of grafting is examined in a scanning electron microscope. Homopolymer was observed as spherical-shaped particules deposited on the surface of cell walls. Coral- and spongelike shaped graft polyacrolein made its appearance after the removal of the homopolymer by the extraction with the pyridine–water mixture. Wrinkles which were observed in the noncopolymerized sample were interpreted as a result of the formation of voids by dissolving the oxidatively degraded cell wall materials in the pyridine–water and the subsequent collapse of the voids and shrinkage of the cell walls on drying. The wrinkle formation was minimized in the case of the copolymerized samples because of the restriction of the shrinkage of the cell wall by the presence of graft polymer in the cell wall.

INTRODUCTION

Chemical process of solid wood and lignocellulosic materials causes some alterations in the cells. In the process, chemicals adhere or bind to surfaces, fill voids, and in some cases degrade components of the wood cell wall. These alterations are induced typically by graft polymerization of those materials with vinyl monomers. In the past, the microscopic investigations of the morphology and structure of so-modified cellulosic fibers or wood have been preferably done by several workers.[1-5]

The xanthate method of grafting developed by Faessinger and Conte[6] has been successfully applied to producing the acrolein copolymer with powdered beech wood.[7] The previous paper[7] suggests that some wood components decompose during the process, in which the wood was treated successively with a dilute aqueous alkali, carbon disulfide, a dilute aqueous Mohr's salt, an aqueous hydrogen peroxide solution, and acrolein monomer. The decomposition resulted in the weight loss on the extraction with the pyridine–water mixture.

Furthermore, the behavior of the graft polyacrolein onto wood to hydroxylamine supports the interpretation that the graft polyacrolein extends from the transient capillaries formed by the swelling action of water to the microscopically visible macropores.[8]

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This paper now relates the morphological and structural changes of cell walls in the grafting process using this method and the behavior of graft and homopolyacrolein as revealed microscopically.

EXPERIMENTAL

Materials

Wood meal used in this work was prepared from beech wood (*Fagus crenata*). The powdered beech wood (40–60 mesh) was extracted successively with hot water for 5 h, and the ethanol–benzene mixture for 48 h before the copolymerization procedure was applied.

Copolymerization

The details of the copolymerization procedure have been described in a previous paper.[7] The wood powder extracted successively with hot water and ethanol–benzene was soaked in an aqueous solution of sodium hydroxide (3%) for 2 h at 25°C with occasional stirring and collected by filtration. The powder collected was treated with carbon disulfide vapor for 2 h at 25°C, placed in a reduced pressure to remove the excess carbon disulfide, washed with a dilute sulfuric acid solution (pH 4) until the washing was no longer yellow, and then ion-exchanged with a 0.0182% ferrous ammonium sulfate (Mohr's salt). The ion-exchanged powder was washed with cold water, soaked in an aqueous solution of hydrogen peroxide (4.5 or 5.5%), collected by filtration, and copolymerized with acrolein monomer for 5 h at 50°C. Finally, the copolymerized wood powder was suctioned to remove the unreacted monomer.

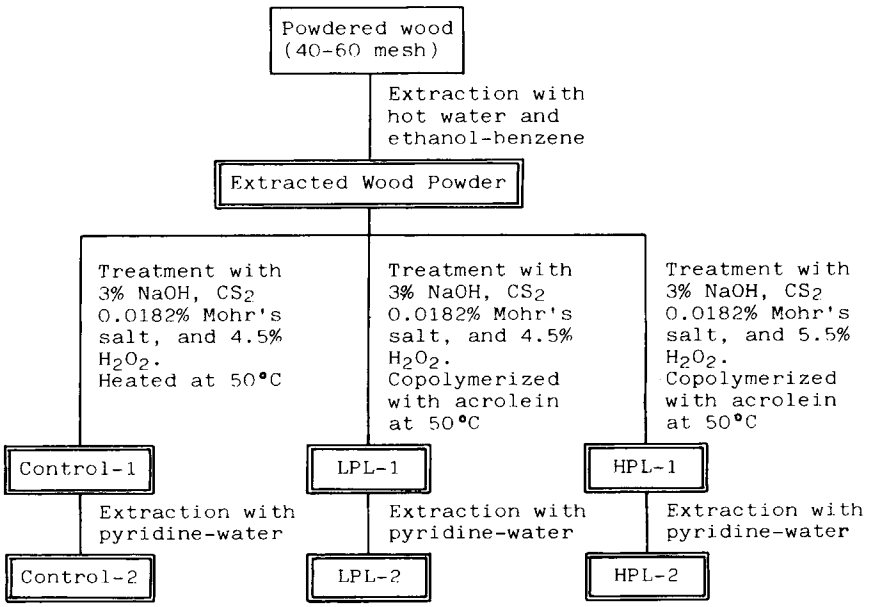

Fig. 1. Flowsheet describing the preparation of seven different samples for microscopic studies.

TABLE I
Degree of Polymer Grafting and Content of Homopolymer of Copolymerized Wood Samples

Samples	Degree of polymer grafting (%)	Content of homopolymer (%)
LPL-1	14.4	0.7
LPL-2	14.4	—
HPL-1	64.7	5.1
HPL-2	64.7	—

Extraction

The homopolymer in the copolymerized samples was extracted with the pyridine–water mixture (65 : 35) for 54 h at room temperature. Noncopolymerized sample as control was treated with the mixture in a similar manner as above.

Preparation for Microscope

Seven different samples prepared for microscopic studies are described in Figure 1. The values for polymer-grafting and homopolymer content of copolymerized samples are summarized in Table I.

A scanning electron microscope (Model Hitachi-Akashi) was employed to investigate the fine structure of all seven types of samples. Carbon and thereafter gold were deposited onto the surface of seven samples in the usual way.

RESULTS AND DISCUSSION

Micrographs of each sample are presented at magnifications of 1000 × and 5000 × in Figures 2–15, and discussed below.

Extracted Wood Powder

Photographs of powdered wood sample extracted successively with hot water and ethanol–benzene are shown in Figures 2 and 3. The torn edges which seem to be in accordance with fibril orientation around pits are sharp.

The rough surface happened to be observed at the lower side of the photograph (Fig. 3), which would probably result in peeling off of cell wall fragments.

Control-1

Figures 4 and 5 show that the torn edge of the cell wall is somewhat folded. This phenomenon indicates that the cell walls have been softened by the successive treatments with 3% solution of sodium hydroxide, carbon disulfide vapor, 0.0182% solution of Mohr's salt, and 4.5% solution of hydrogen peroxide. Of these processes, the treatment with hydrogen peroxide at 50°C will particularly contribute to the cleavage of the cell wall materials. In this

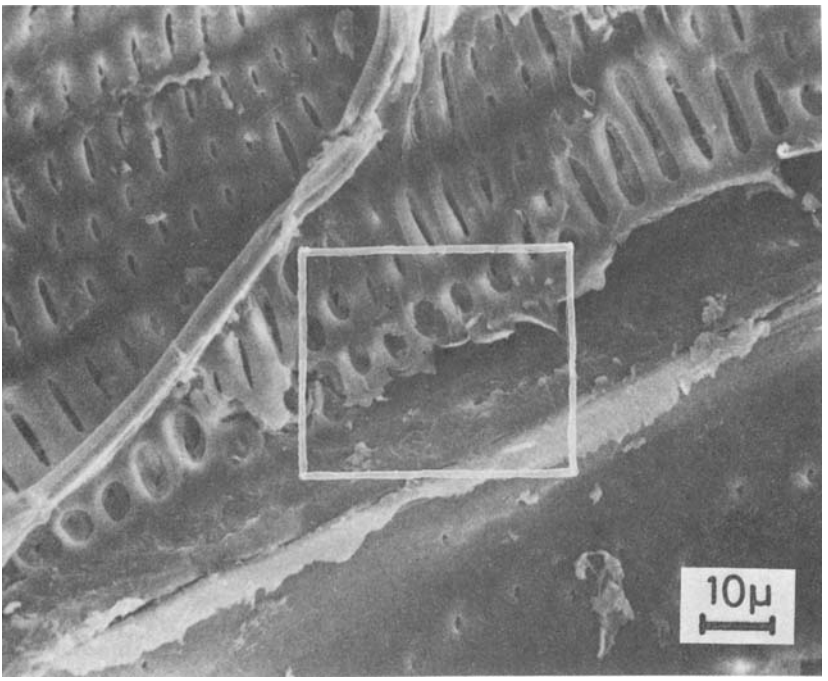

Fig. 2. An overall view of the extracted wood powder (1000 ×).

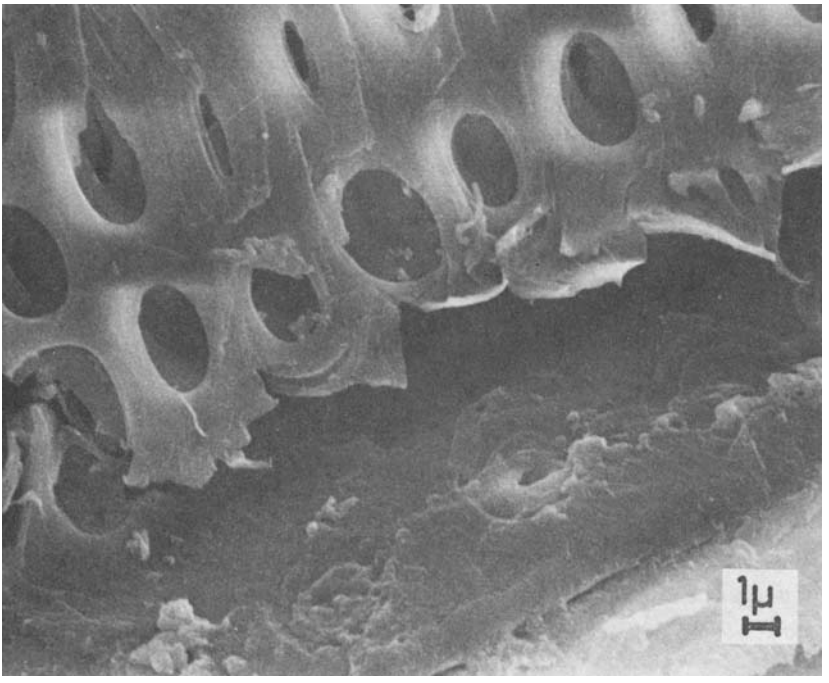

Fig. 3. A fine view of the extracted wood powder (5000 ×).

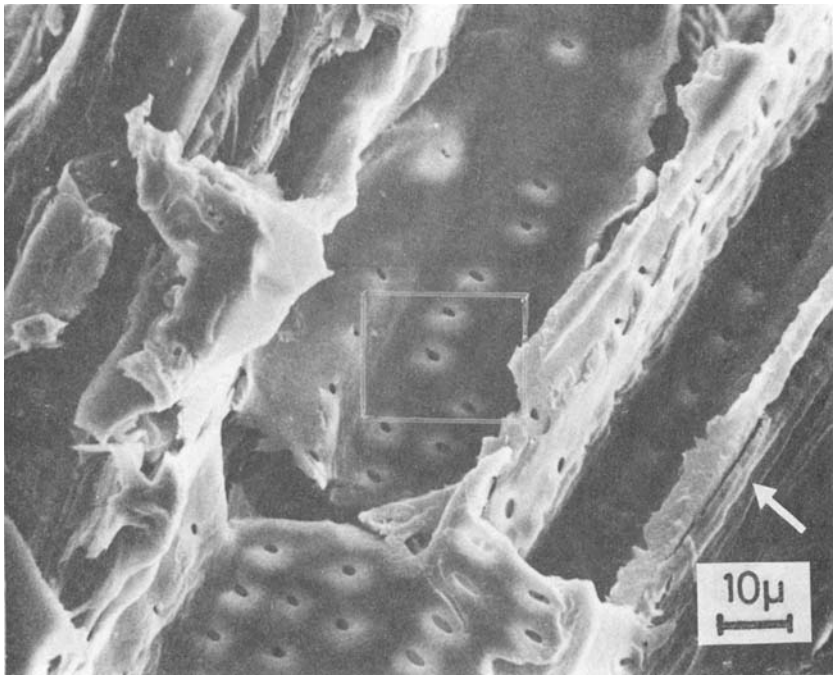

Fig. 4. An overall view of control-1 (1000 ×).

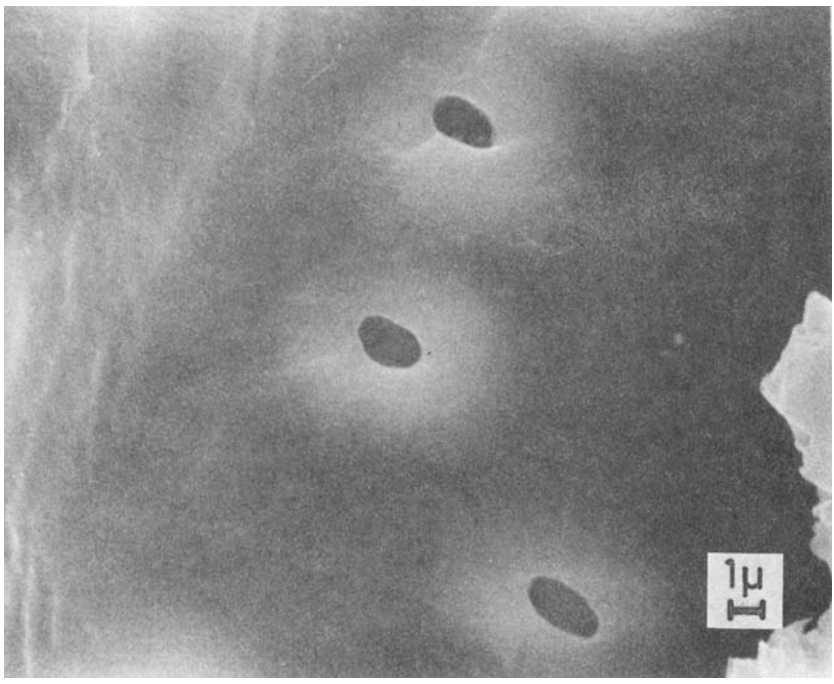

Fig. 5. A fine view of control-1 (5000 ×).

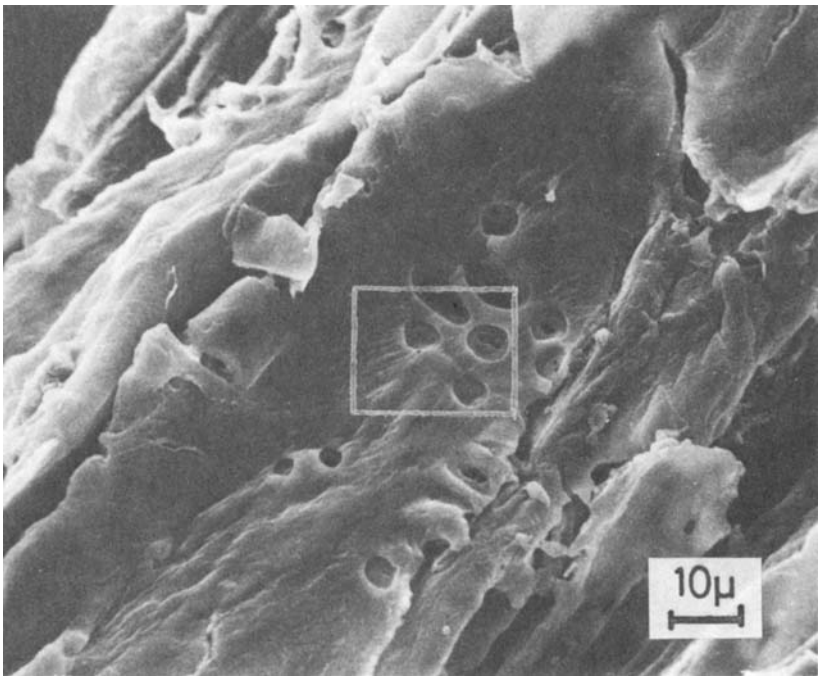

Fig. 6. An overall view of control-2 (1000 ×).

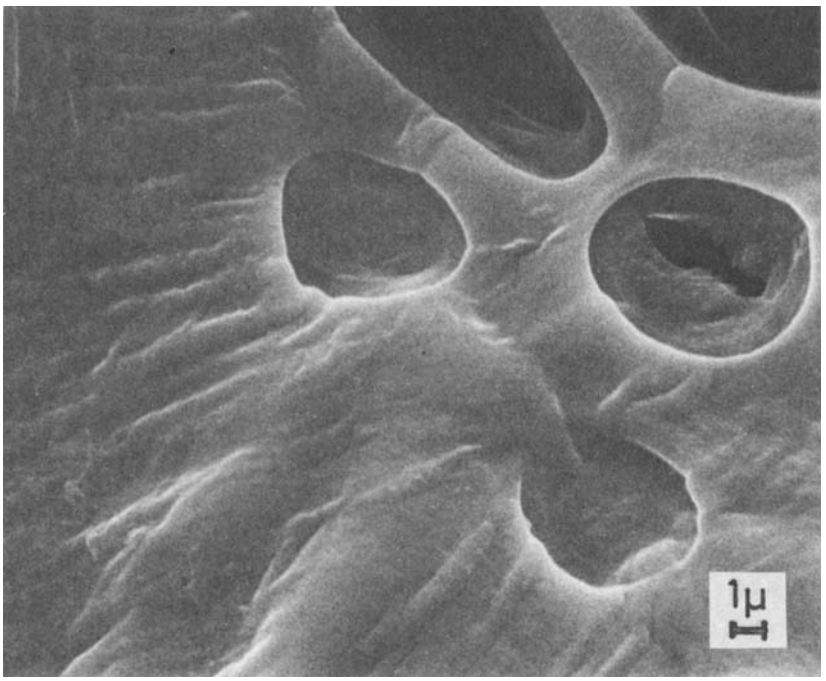

Fig. 7. A fine view of control-2 (5000 ×).

regard, Hornof and Puissant[9] noted that increasing the peroxide concentration produces a side effect by causing oxidative degradation of cellulosic material. Lonikar et al.[10] recently described that the break of the intermolecular bonding of lignin and interpolymer bonds among the main components of wood results in loosening of wood structure as well as delignification. Furthermore, the detachment of intercells or cell walls marked with an arrow in Figure 4 may be an evidence of structural loosening of cell walls.

Control-2

The morphological difference between control-1 and 2 shown in Figures 5 and 7, respectively, is obviously the wrinkles appeared in control-2. The previous paper pointed out that the weight loss on the extraction with the pyridine–water mixture is not only by the loss of homopolymer but also by the loss of wood components.[7] The loss of the main components creates voids in the cell wall.[11] As a result of collapse of the voids and shrinkage of cell wall on drying, the cell wall wrinkles.

LPL-1

The rough surface of LPL-1 sample shown in Figures 8 and 9 indicates the deposition of particles that are assumed to consist of the acrolein homopolymer. It will be shown in the next section that the deposits are not the graft polymer. The remarkable wrinkles are not found on the cell wall, because the LPL-1 sample has not been extracted with the pyridine–water mixture.

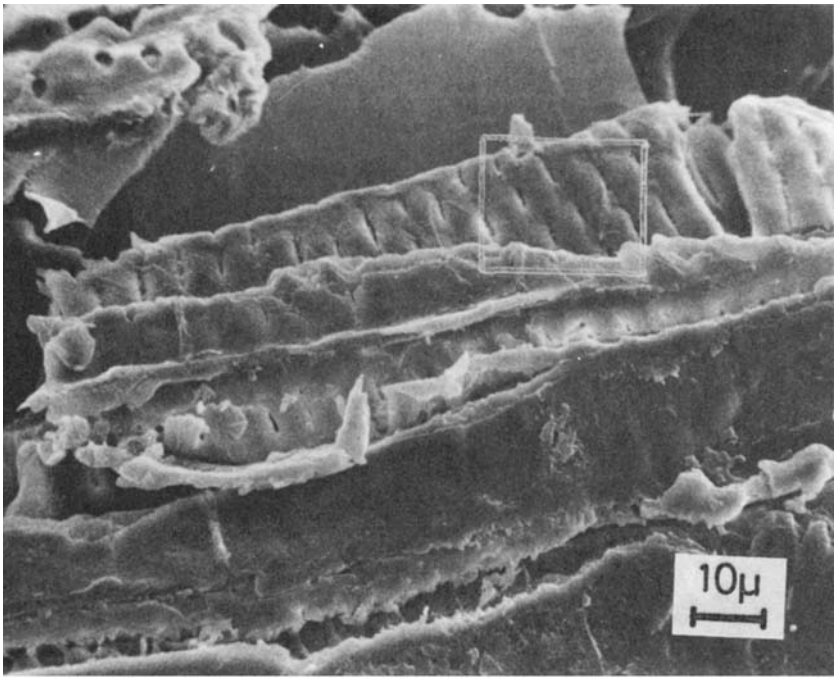

Fig. 8. An overall view of LPL-1 (1000 ×).

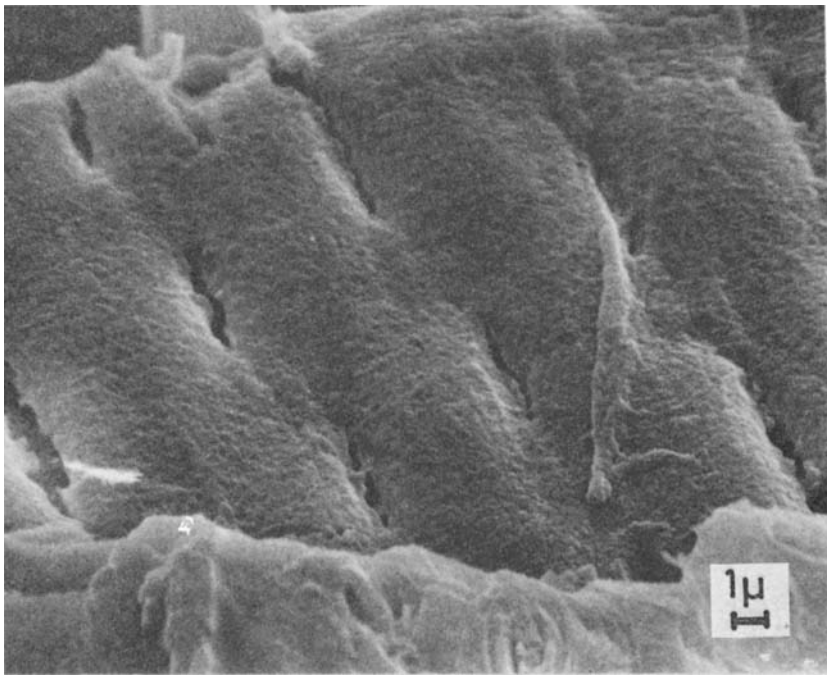

Fig. 9. A fine view of LPL-1 (5000 ×).

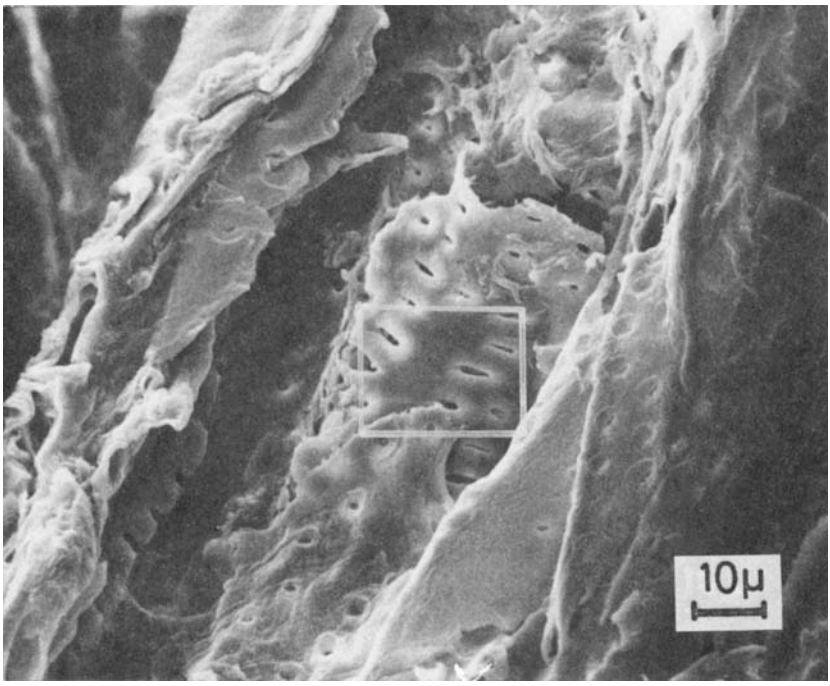

Fig. 10. An overall view of LPL-2 (1000 ×).

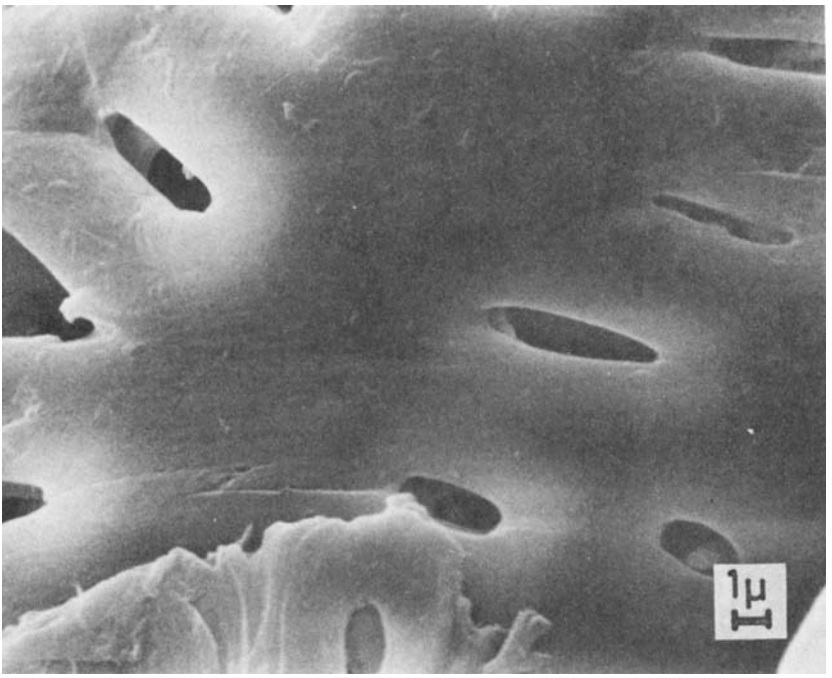

Fig. 11. A fine view of LPL-2 (5000 ×).

LPL-2

After the removal of the homopolymer at 15.1% polymer loading (LPL-1), the particles described in the above section are no longer observed as shown in Figures 10 and 11. This fact supports the view that the graft polymers have mingled within the cell walls. Taking into account of the void volume of the transient capillaries (about 0.3 mL/g, in the case of wood), the graft polymer at the level of 14.4% grafting should be accommodated in the capillaries.

Wrinkles are observable but not so remarkable as control-2. This difference can be interpreted as a restriction of collapsing voids on drying by the presence of graft polymer in the transient capillaries of the cell walls.

HPL-1

Figures 12 and 13 are the surface of HPL-1 sample that shows the expected rough surface as observed in LPL-1. But the particles deposited on the surface are larger and more abundant in HPL-1 than in LPL-1, because the content of homopolymer is greater in HPL-1 than in LPL-1 as indicated in Table I.

HPL-2

Both Figures 14 and 15 are the surface of the HPL-2 sample that show the sponge- and coral-like structures which are conspicuously revealed with the removal of homopolymer. One of the reasons for the formation of the porous structure would be the release of gaseous products during the grafting copolymerization. The other possible reason is the removal of the decomposed cell

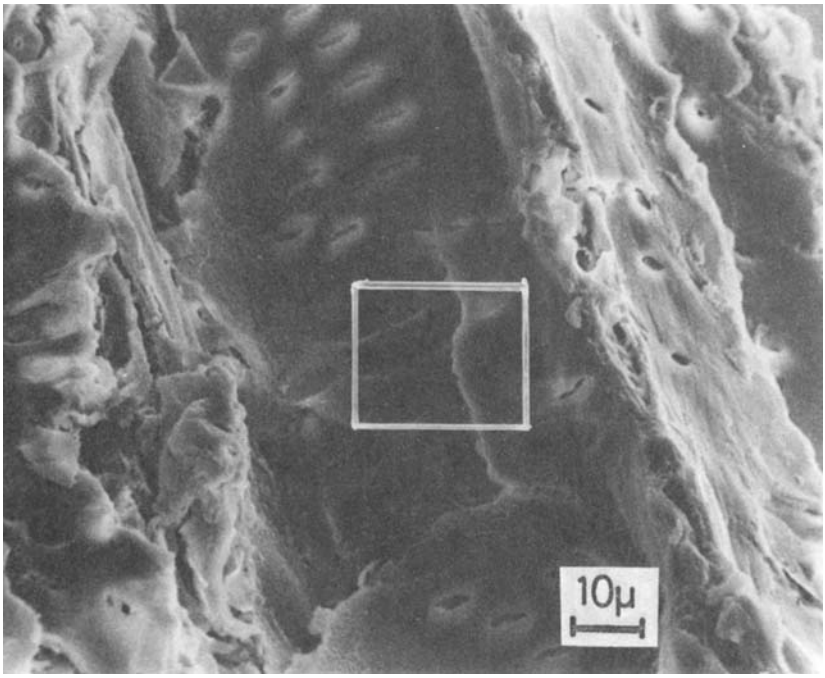

Fig. 12. An overall view of HPL-1 (1000 ×).

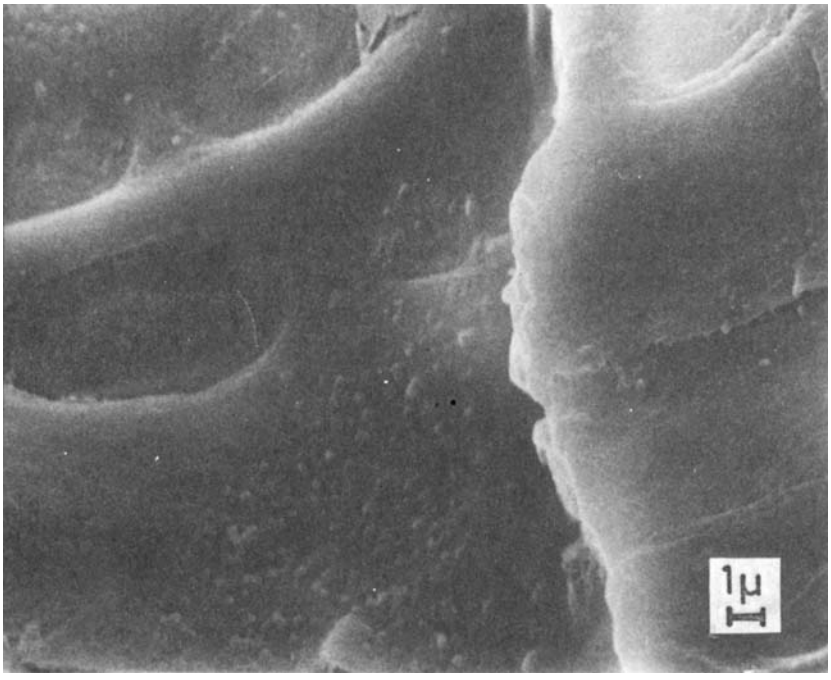

Fig. 13. A fine view of HPL-1 (5000 ×).

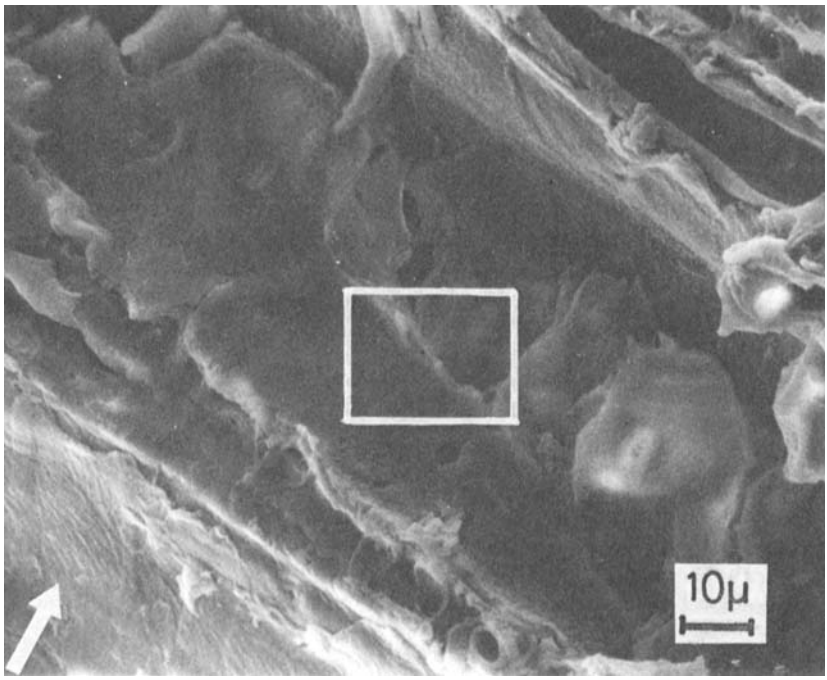

Fig. 14. An overall view of HPL-2 (1000 ×).

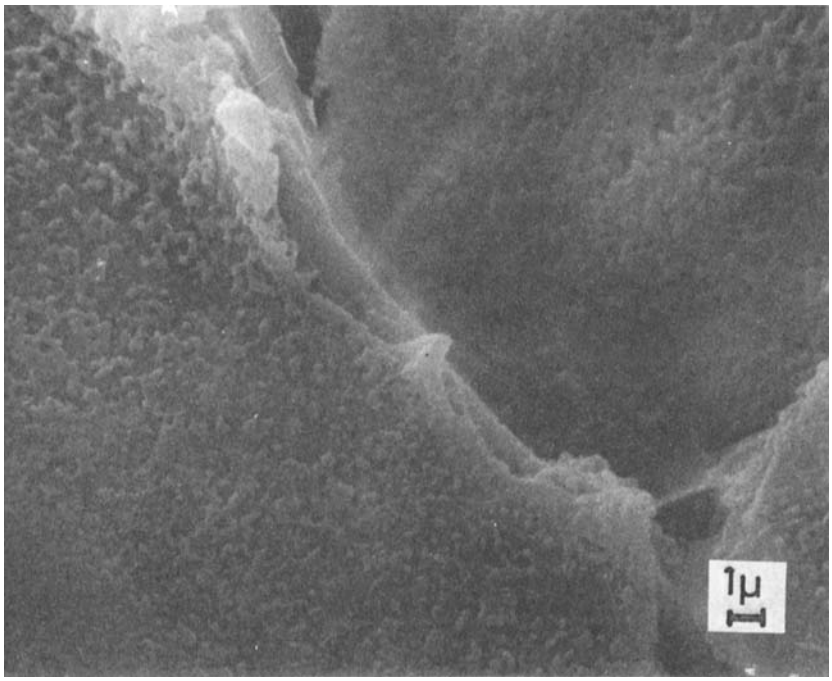

Fig. 15. A fine view of HPL-2 (5000 ×).

wall materials which have been mingled in the graft polyacrolein. The latter view is supported by the fact that the dissolution of the decomposed wood components was obstructed to some extent by the graft polyacrolein.[7]

Considering the high degree of grafting (64.7%), the porous structure should be the graft polyacrolein which extends to the microscopically visible macropores as suggested in the previous paper.[8] No obvious wrinkles are noticeable in Figure 14 except for an area indicated with an arrow. In this area, neither sponge- nor coral-like structure is observed, which means that the grafting reaction does not uniformly occur under the condition employed. The graft polymer in the voids of cell walls, therefore, plays a role in restriction of shrinkage of cell walls on drying.

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