

# Effect of Corona Discharge Treatment on Cellulose Prepared from Beech Wood

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## Synopsis

Cellulose prepared from beech wood (*Fagus crenata* Blume) was treated in a corona discharge. The chemical changes produced by the treatment were investigated by use of infrared spectrum, Schiff's reaction, adsorption of methylene blue and Orange II, and intrinsic viscosity. Infrared absorption bands at 1382 and 1715  $\text{cm}^{-1}$  were formed. The color reaction with Schiff's reagent indicated that the 1715  $\text{cm}^{-1}$  absorption was due to the aldehyde group and not to the carboxyl group. The intrinsic viscosity was decreased by the air corona treatment, but was not affected by nitrogen corona treatment. The adsorption of methylene blue was not increased by corona treatment, indicating that no acidic groups were formed. Adsorption of Orange II indicated that some basic groups were formed by the nitrogen corona after a long treatment time. Low molecular weight fractions showing the 1382  $\text{cm}^{-1}$  infrared absorption band were formed by corona treatment. These fractions were removed from cellulose by washing with water, and they increased with an increase in the treatment time. The absorption band at 1382  $\text{cm}^{-1}$  was assigned to the symmetric carbon-hydrogen bending of methyl group.

## INTRODUCTION

Corona discharge is used for the surface activation of synthetic polymers and woods. For example, polyethylene film is treated by corona discharge before printing,<sup>1</sup> and graft polymerization of vinyl monomer or ethylene imine to wood can be initiated by corona treatment.<sup>2,3</sup>

Surfaces of wood containing a high concentration of extractives are often hydrophobic. Heat treatment of the surface can produce the same effect. When such woods are glued with water-borne adhesives, delaminations occur frequently. Improved gluing of these woods has been achieved by use of corona treatment, but joint strength decreased with increase in the treatment time.<sup>4-6</sup> When thin sections of wood were corona treated, the tensile strength of the sections decreased.<sup>7</sup> Here it seemed likely that the cellulose, one of the main component of wood, was degraded.

It proved difficult to detect any chemical changes due to the corona treatment of cellulosic materials. Therefore, Schiff's color reaction<sup>8</sup> and the adsorption of methylene violet and Orange II<sup>9</sup> were tried as sensitive methods for detection of corona-induced chemical changes.

In this study, cellulose isolated from wood was corona treated, and the decrease in the molecular weight of the cellulose and the formation of new groups were investigated.

## EXPERIMENTAL

### Cellulose

Beech (*Fagus crenata* Blume) wood meal (40–80 mesh) was extracted with alcohol–benzene and was delignified by the chlorite method.<sup>10</sup> The holocellulose was extracted with 24% aqueous potassium hydroxide to remove the hemicellulose components. The cellulose obtained was then washed with water, neutralized with acetic acid, rewashed with water and dried in air.

### Corona Treatment

The cellulose sample was conditioned at 20°C and 72% relative humidity. Corona electrodes were disks 105 mm in diameter set parallel to each other, 8 mm apart. Two glass plates (1.8 mm thick) were used as insulators between the electrodes.<sup>4</sup> Cellulose samples were placed on the glass plate set on the lower electrode. The applied potential was 15.0 kV, with a frequency of 60 Hz. The atmosphere for the discharge was either dry air or nitrogen.

### Infrared Spectrum

Infrared spectra were taken with a Shimadzu IR-27G recording spectrophotometer by use of the KBr pellet method.

### Reaction with Schiff's Reagent and Measurement of Color Difference

One gram of basic fuchsin was dissolved in 100 mL of boiling water, and 20 mL of 1 *N* hydrochloric acid solution was added at 50°C. Then, at 25°C, 1 g of sodium hydrogen sulfite was dissolved. This solution was used for Schiff's reaction after standing 3 or 4 days.<sup>11</sup>

The degree of color development was determined by the method of JIS color difference. The spectral reflectance of the specimen compared to that of a magnesium oxide plate were recorded with a Shimadzu UV-200 recording spectrophotometer to which the integrating sphere was attached; chromatic values of a specimen were then calculated by JIS Z 8722-1971. The difference in color between the control and the corona-treated specimen was calculated in a *Lab* system by JIS Z 8730-1970.

### Adsorption of Methylene Blue

Aqueous sodium hydroxide (N/100) was used as the solvent for methylene blue. The initial concentration of methylene blue was  $5.3 \times 10^{-6}$  mol/L, and the ratio of methylene blue solution to cellulose was 20. Adsorption time was 24 h at room temperature. The concentration of methylene blue in the supernatant was determined by the 618-nm absorbance, and the adsorption on the cellulose calculated by difference.

### Adsorption of Orange II

Aqueous hydrochloric acid (N/100) was used as the solvent for Orange II. Initial concentration was  $5.2 \times 10^{-5}$  mol/L, and the other conditions were the

same as those for methylene blue except that the concentration in the supernatant liquid was determined by the 484-nm absorbance.

### Nitration of Cellulose and Viscosity

Corona-treated celluloses were nitrated with a mixture of fuming nitric acid and phosphorous pentoxide<sup>12</sup> at 0°C. Nitrated cellulose samples were dissolved in acetone, and intrinsic viscosity was measured at 25°C.

### X-Ray Diffraction

X-ray diffractograms of specimens were recorded using a Rigaku Geigerflex 2013 X-ray diffractometer to which a monochromator was attached. The diffraction intensity was measured from  $2\theta = 10^\circ$  to  $2\theta = 30^\circ$  to include the three main diffraction maxima of the cellulose II lattice structure: the (101), (10 $\bar{1}$ ), and (002) planes. The percent crystallinity is defined by

$$\text{Crystallinity} = 100(I_{002} - I_{am}) / (I_{002})$$

where  $I_{002}$  is the intensity of the diffraction from the (002) plane at  $2\theta = 21.9^\circ$  and  $I_{am}$  is that of the background scatter measured at approximately  $2\theta = 18.0^\circ$ . The specimens were tested three times and the mean taken.

## RESULT AND DISCUSSION

### Infrared Spectrum

The infrared spectra of the cellulose samples in this study are shown in Figure 1. Spectra taken on cellulose treated up to 120 min in a nitrogen corona were the same as for the untreated control.

In contrast, in the case of air corona, the band in  $1382\text{ cm}^{-1}$  is detectable at 60 min treatment, and its absorbance increased with increasing treatment time (90 and 120 min in air). This  $1382\text{ cm}^{-1}$  band was previously found on corona-treated hemicellulose, dioxane lignin of beech, and on hydroxyethylcellulose.<sup>13</sup> And, its absorbance increased with an increase in the degree of treatment.

Several authors have reported that the C=O stretching absorption band ( $1730\text{ cm}^{-1}$ ) is found in woods or celluloses treated by a corona discharge.<sup>4,7,14</sup> The results in Figure 1 support these findings. Also the increase in the absorbance with time of treatment is similar to the trend reported previously.<sup>4</sup>

### Schiff's Reaction

The infrared analysis showed that a small amount of carbonyl group had been formed by the corona treatment.<sup>4-7,15,16</sup> To determine whether the carbonyl group was aldehyde or carboxyl, the color produced by the addition of Schiff's reagent was examined.<sup>8</sup> Schiff's reagent is known to be sensitive to the presence of aldehyde group in wood.

The difference in color between the control and the corona-treated cellulose after Schiff's reaction was plotted against the treatment time in Figure 2. The increased color with increase in the treatment time indicates that the aldehyde

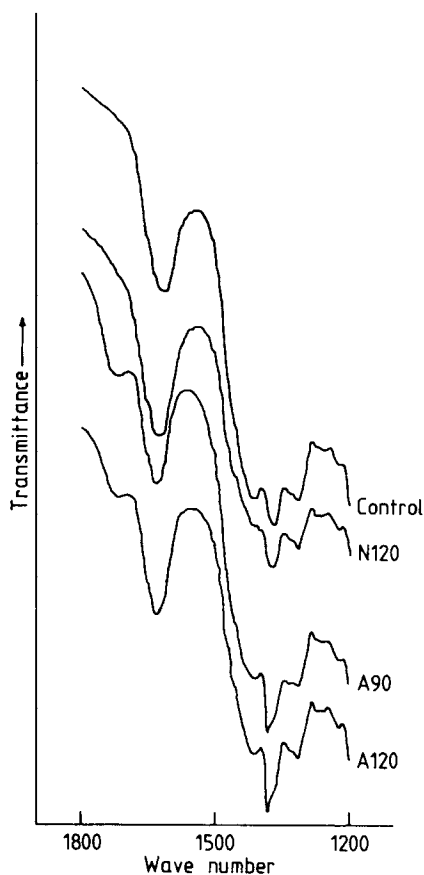


Fig. 1. Infrared spectra of corona-treated cellulose. Control: nontreated cellulose; N120: 120 min in nitrogen; A90: 90 min in air; A120: 120 min in air.

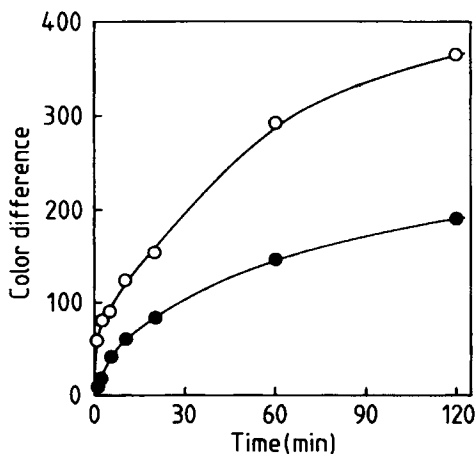


Fig. 2. Color difference between control and corona-treated cellulose with Schiff's reagent. O: air; ●: nitrogen.

group content of the cellulose was increased by treatment in the discharge. It is interesting to note that the increment of color for the nitrogen corona was half that for the air corona.

### Methylene Blue Adsorption

Aldehyde groups are often unstable, and easily converted to carboxyl groups by autoxidation. If carboxyl groups are thus produced on cellulose by corona treatment, they might be detected by the adsorption of basic dyes such as methylene violet or methylene blue.<sup>8,9</sup>

As shown in Figure 3, the amount of methylene blue adsorbed on corona-treated cellulose was constant (ca.  $1.01 \times 10^{-7}$  mol/g) for times of treatment up to 120 min in both air and nitrogen coronas. These results suggest that acidic groups were not formed by the corona treatment, and that the aldehyde groups that were formed did not change to carboxyl groups.

### Orange II Adsorption

The possible formation of basic groups by corona treatment was investigated by use of the acidic dye, Orange II, which would be expected to adsorb onto positively charged sites on the cellulose. The results obtained are shown in Figure 4.

In the case of the air corona, the amount of Orange II adsorbed was constant. On the other hand, in the case of the nitrogen corona, the adsorption increased with an increase in the corona treatment time from 60 to 120 min, but it was constant up to 60 min treatment. It seems therefore that some basic groups were formed in the nitrogen corona after an extended time of treatment.

### Intrinsic Viscosity

In previous work,<sup>7</sup> the tensile strength of thin sections of corona-treated wood decreased, and degradation of the cellulose was assumed. To clarify this point, the intrinsic viscosity of corona-treated cellulose was measured by means

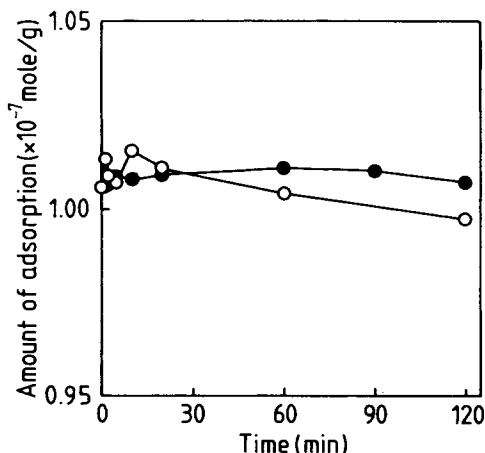


Fig. 3. Adsorption of methylene blue on corona-treated cellulose. ○: air; ●: nitrogen.

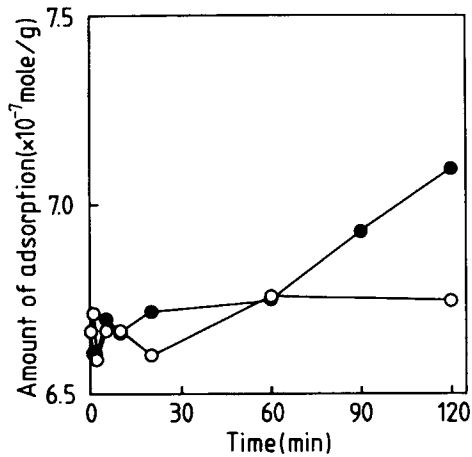


Fig. 4. Adsorption of Orange II on corona-treated cellulose. ○: air; ●: nitrogen.

of the nitration method.<sup>12</sup> As shown in Figures 5 and 6, the intrinsic viscosity increased slightly at an early stage of treatment for both the air and nitrogen coronas. However, there is a marked decrease in intrinsic viscosity for longer treatment times by the air corona. The Huggins' coefficients showed the same trends. The molecular weight of the cellulose control was ca. 335,000 compared with ca. 200,000<sup>17</sup> (intrinsic viscosity = 4) for the cellulose, which was treated for 120 min in air corona.

On the other hand, the intrinsic viscosity and, thus, the molecular weight of the cellulose treated in the nitrogen corona was not decreased as shown in Figure 6. The absence of chain scission indicates that the nitrogen corona is a milder treatment than the air corona. This conclusion is supported by the infrared spectra (Fig. 1) and the color produced by Schiff's reagent (Fig. 2). It is possible that the initial increase in intrinsic viscosity and the Huggins'

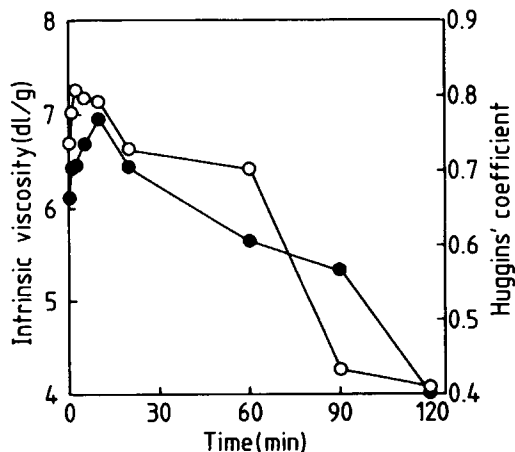


Fig. 5. Intrinsic viscosity and Huggins' coefficient of air corona treated cellulose by nitration method. ○: intrinsic viscosity; ●: Huggins' coefficient.

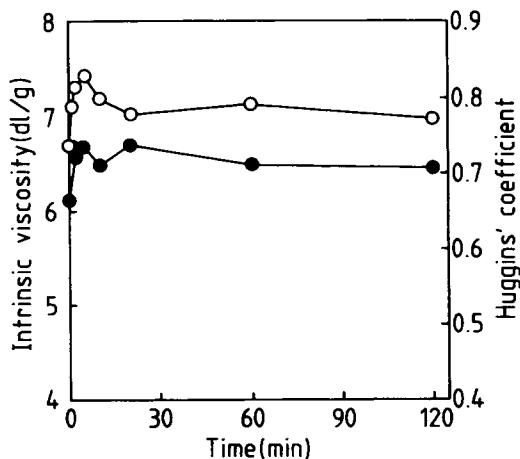


Fig. 6. Intrinsic viscosity and Huggins' coefficient of nitrogen corona treated cellulose by nitration method. ○: intrinsic viscosity; ●: Huggins' coefficient.

coefficient may be caused by crosslinking of cellulose molecules by the corona treatment.

### Crystallinity

The crystallinities calculated from X-ray diffractograms are shown in Figure 7. The data indicate no significant changes in the crystallinity of the corona-treated samples. This was possibly due to the fact that the corona treatment affected only a thin layer on the surface of the cellulose.

### Effect of Washing

Previously, it was found possible to elute the treated layer from corona-treated polyethylene with ethanol.<sup>15</sup> A similar experiment was tried in the pres-

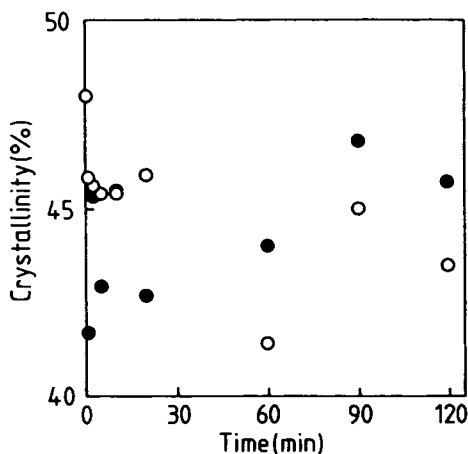


Fig. 7. Crystallinities of corona-treated cellulose calculated from X-ray diffractograms. ○: air; ●: nitrogen.

ent work. The infrared spectrum taken after washing the treated cellulose with distilled water is shown in Figure 8. The characteristic absorption band at  $1382\text{ cm}^{-1}$  disappeared, and absorbance at  $1715\text{ cm}^{-1}$  decreased a little.

Spectra taken after washing with N/20 hydrochloric acid aqueous solution are shown in Figure 9. The spectra were the same as for celluloses washed with water.

Spectra taken after washing with N/20 sodium hydroxide aqueous solution are shown in Figure 10. No difference is seen between the control and the cellulose samples treated in the air corona.

Therefore, it seems that the absorption bands at  $1715$  and  $1382\text{ cm}^{-1}$  produced by corona treatment were formed on the low molecular weight fractions<sup>18</sup> of the cellulose, which were completely eluted by washing in alkali. The proportion of material eluted increased with an increase in the corona treatment time (Fig. 11).

The spectra of the eluted fractions produced by treatment in the air corona are shown in Figure 12. The absorption band at  $1382\text{ cm}^{-1}$  began to appear in the spectrum of the sample treated for 20 min. This band was noted previously in the spectrum of hydroxyethylcellulose<sup>13</sup> and has been assigned to the symmetric carbon-hydrogen bending of the methyl group.<sup>19</sup>

The absorption band at  $1715\text{ cm}^{-1}$  also began to appear in the spectrum of the sample treated 20 min. This band was assigned to the C=O stretching, and shifted from  $1715\text{ cm}^{-1}$  (10–60 min) to  $1720\text{ cm}^{-1}$  at 90 min treatment and to

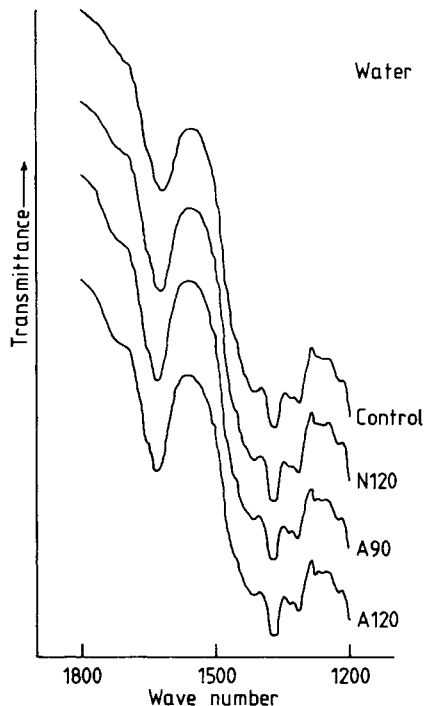


Fig. 8. Infrared spectra of corona-treated cellulose washed with distilled water. Control: non-treated cellulose; N120: 120 min in nitrogen; A90: 90 min in air; A120: 120 min in air.



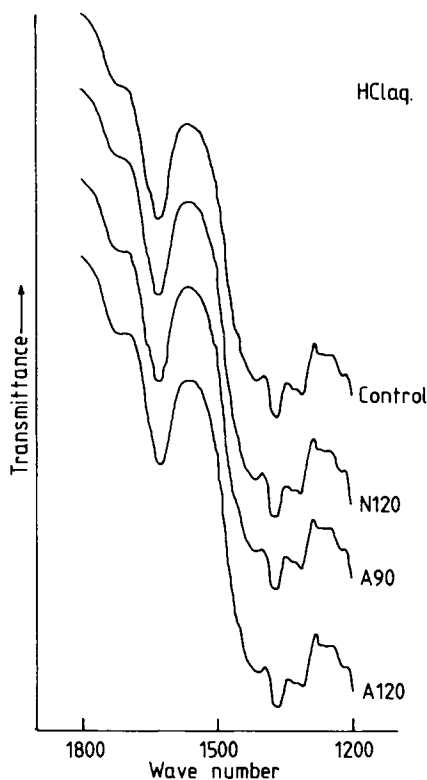


Fig. 9. Infrared spectra of corona-treated cellulose washed with N/20 hydrochloric acid aqueous solution. Control: nontreated cellulose; N120: 120 min in nitrogen; A90: 90 min in air; A120: 120 min in air.

1725  $\text{cm}^{-1}$  at 120 min treatment. Perhaps the increased steric hindrance between the carbonyl group and its neighbors contributed to this shift.

Absorption bands at 2400, 820, and 760  $\text{cm}^{-1}$  in the eluted fractions increased with an increase in the treatment time; such increments were not detected in spectra of whole treated samples. Absorption bands at 890, 830, and 700  $\text{cm}^{-1}$  decreased greatly in the fractions eluted from cellulose treated in the air corona. The absorption band at 890  $\text{cm}^{-1}$  was assigned to carbon-hydrogen bending at the  $\text{C}_1$  position of the glucose residues. Such an effect would be expected if the eluted material was low molecular weight cellulose. Absorption bands at 830 and 700  $\text{cm}^{-1}$  were assigned to carbon-hydrogen deformation and oxygen-hydrogen out-of-plane bending, respectively.

The spectrum of the material eluted from cellulose samples treated in the nitrogen corona is also shown in Figure 12. The increase of the absorption band at 1382  $\text{cm}^{-1}$  was the same as that of air corona treated cellulose. The absorption bands at 830 and 700  $\text{cm}^{-1}$  disappeared, while the bands at 890 and 760  $\text{cm}^{-1}$  did not change. These results indicate no change in the carbon-hydrogen bending at the  $\text{C}_1$  position and support the previous result that the molecular weight of the cellulose was essentially unchanged by treatment in the nitrogen corona (see Fig. 6).

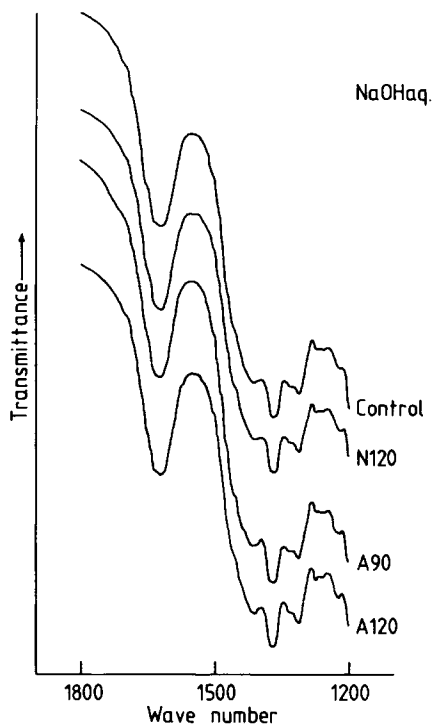


Fig. 10. Infrared spectra of corona-treated cellulose washed with N/20 sodium hydroxide aqueous solution. Control: nontreated cellulose; N120: 120 min in nitrogen; A90: 90 min in air; A120: 120 min in air.

### CONCLUDING REMARKS

This work shows that the air corona treatment lowers molecular weight of cellulose and oxidizes celluloses to produce aldehyde groups and not carboxyl

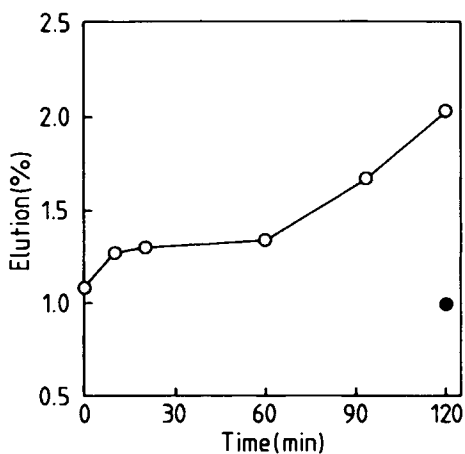


Fig. 11. Elution fraction of corona-treated cellulose by distilled water. ○: air; ●: nitrogen.

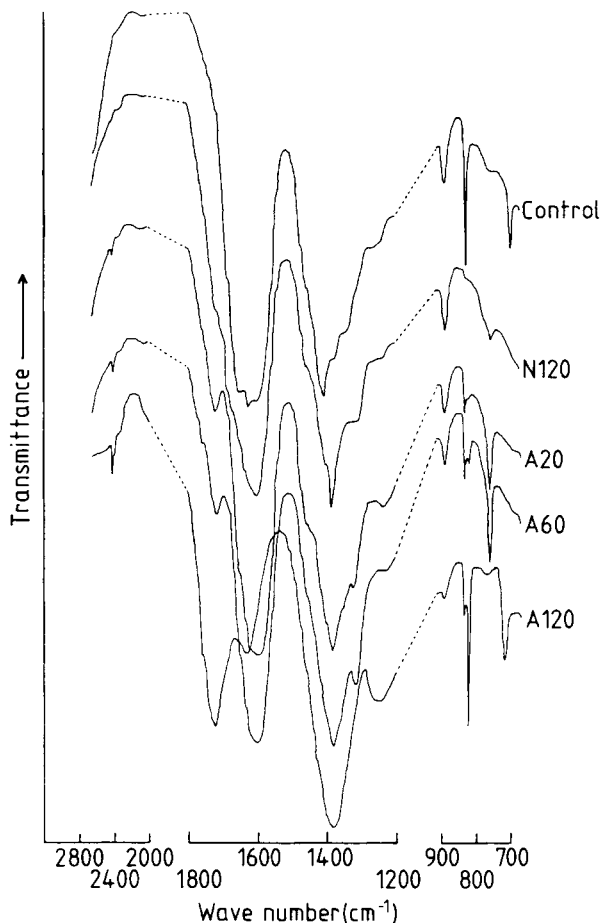


Fig. 12. Infrared spectra of treated layer eluted with water from corona-treated cellulose. Control: nontreated cellulose; N120: 120 min in nitrogen; A20: 20 min in air; A60: 60 min in air; A120: 120 min in air.

groups. Some low molecular weight materials that have  $1382\text{ cm}^{-1}$  infrared absorption band are produced and are removed by washing with water. The intrinsic viscosity data indicate that decreases in molecular weight may occur throughout a major fraction of the cellulose by the chain scission in corona discharges. The decrease in C-H bending absorption at the  $C_1$  position agrees with the trend of molecular weight changes. The steric hindrance between the aldehyde groups produced and its neighbors increased.

Nitrogen corona produces no significant changes in intrinsic viscosity and in infrared spectra, and is milder than air corona as shown by the color reaction of Schiff's reagent. The small color reaction detected after treatment in a nitrogen corona may be due to subsequent oxidation in air of the active sites produced in the corona. Furthermore, some basic groups are formed by the nitrogen corona after lengthy treatment.

In the previous work, the wood joint strength glued with urea-formaldehyde resin was improved by air corona treatment of wood surfaces, from 93.5 to 115.8

kgf/cm<sup>2</sup>. Also lowering of the joint strength caused by the heat treatment of wood was recovered by corona treatment.<sup>4</sup> These improvements in the joint strength were accompanied by an increase in the wettability. It seemed that the increasing wettability of corona-treated wood resulted from the surface oxidation.<sup>4</sup>

Despite little production of aldehyde groups, the nitrogen corona improved the bond strength of wood.<sup>6</sup> The absence of chain scission in the nitrogen corona meant that there was no degradation in the strength of wood. This gives treatment in nitrogen an advantage over treatment in air.

The purpose of the work reported in the present study was to establish the mechanism of surface oxidation by corona treatment. Evidence of chemical changes and chain scission was also found.

Future work will deal with the effect of corona treatment on lignin, which is one of the main components of wood. For some applications, we are studying the introduction of functional groups to cellulosic materials by means of reactions with aldehyde groups produced by the corona treatment. For example, coupling of phenylhydrazine or semicarbazide compounds with aldehydic groups generated by the discharge could produce new and useful derivatives of cellulose.

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