Improvement of Plybond Strength of Paperboard by Corona Treatment

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SYNOPSIS

It was found that the treatment of the surfaces of wet pulp sheets (moisture content; up to 85%) in a corona discharge improved greatly the plybond strength of the paperboard obtained when the treated wet pulp sheets were laminated together, pressed, and then dried. Treatment was carried out by use of a corona apparatus which had variable driven roll electrodes for transporting the wet pulp sheets through a corona field and was attached to a high-voltage generator (~ max 500 W, ~ 16 kV at 5 kHz). The plybond strengths of the paperboards were examined by means of Tappi RC-273 and JIS P8139 methods. Some experiments regarding the chemical effects of the corona treatment on the surface modification of wet pulp sheets were made with the aid of dye adsorption methods. Both untreated and corona-treated pulps adsorbed basic dyes, methylene blue, etc., with the same extent of dyeing. This indicates that no measurable acidic sites (carboxyl groups) increased on the surfaces of the pulp sheets during the corona treatment. To detect aldehyde groups, the dyeing examination of the pulps with Schiff's reagent was made, and the results showed a higher dyeing ability for the corona-treated pulps compared to the untreated, indicating that aldehyde groups on the pulp surfaces increased with an increase in the degree of corona treatment. The corona treatment seems to produce on the surface layer lightly oxidized and fairly degraded polysaccharide chains, which will tend to swell in water and thus act as an adhesive in plybonding the pulp sheets.

INTRODUCTION

Corona discharge treatment is one of the interesting techniques for surface modification of polymers and is commonly used in plastic films industry. The adhesive properties, printability, and other properties of polymer film surfaces markedly improve with a corona treatment. In spite of the fact that this method of surface modification is commonly used industrially, there is still some controversy over the mechanism of the process.

The strong bond developed in paper after its formation on the paper machine is generally attributed to the hemicelluloses on the surface of the fibers. One way of increasing the bonding capacity of cellulose fibers is to change the cellulose surface so that the new surface possesses properties similar to those of hemicellulose.

Goring and co-workers[1-4] treated cellulose materials and wood veneer in a corona discharge and found that the treatment increased the bond strength. However, the tensile strength did not change substantially, indicating that the corona treatment altered the surface only. Goring[1] also reported that the presence of a small amount of moisture in the sample is found to be essential.

The cause of this corona effect is still not clear, although Goring[1,5] has thought that the effect is probably due to oxidative degradation of the cellulose molecules near the surface. A similar explanation for the effect of corona treatment on cellulose has been proposed by Brown and Swanson,[6] who relate the improved bonding to changes in the solid surface free energy accompanying the treatment. This change was claimed to be caused by an increase in the polarity of the surface, which was observed to be more hydrophilic after the treatment.

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The purpose of the present work was to apply such a corona treatment to improvement of the plybond strength of the paperboard obtained when wet pulp sheets were lap joined together, pressed, and then dried.

It was found that the corona treatment of the surfaces of wet pulp sheets having moisture content of up to about 85% greatly improved the plybond strength. In addition, some experiments concerning the chemical effects of the corona treatment on the surface modification of wet pulp were made by dye adsorption methods, and some tentative explanations were offered for the cause of the effect.

EXPERIMENTAL

Corona Treatment

The corona treatment apparatus is shown in Figure 1. This apparatus has variable driven roll-electrodes made of stainless steel. The upper electrode is coated with a dielectric layer of silicon rubber and is supplied by alternating high voltage generator with maximum 500 W and 16 kV at 5 kHz. The lower electrode is grounded. The gap between the two electrodes is adjusted to 3.2 mm. The wet pulp sheets on the copper plate is treated by transporting through a corona discharge field. Both the rotation speed of the roller and the electric power of the high voltage generator are variable.

The degree of treatment is given as shown in the following equation:

$$\text{degree of treatment} = \frac{W}{V \times L} \quad (\text{W min/m}^2)$$

where W is the electric power (W), V is the speed of treatment (m/min), and L is the length of electrode (m), constant at 0.5 m. The corona treatment was carried out in an atmosphere of dry air or nitrogen.

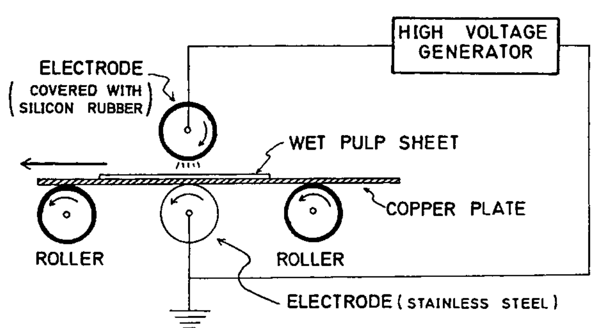

Figure 1 Diagram of corona treatment apparatus.

Measurement of Plybond Strength

The pulp sheets were made from commercial bleached kraft pulps (BKP) of softwood and hardwood with the use of a Tappi standard sheet machine in the usual way. The basis weight of the pulp sheets was 60 g/m^2.

After corona treatment, the pulp sheets were lap-joined together and pressed for 7 min at a pressure of 3.5 kg/cm^2 and then dried for 10 min at the temperature of 105°C.

The bonded specimens were then moisture-adjusted under standard conditions and the measurement of the plybond strength of them was carried out with the Tappi method[7] and the JIS method,[8] as shown in Figure 2.

Water Absorptiveness and Moisture Regain

Both the face and back of the paper were coated with polypropylene tack tapes and the test specimens were soaked in water for 2 min at 25°C. The water absorptiveness was expressed as weight increase caused by the water absorption from the side of the specimens.

The hydroscopic properties of the corona-treated pulps were also examined. The specimens were first vacuum-dried, and then they were subjected to humidification at various relative humidities in rooms of constant temperature, 20°C. The moisture adsorption was estimated from the weight increase of the specimens.

Dye Adsorption

The chemical effects of the corona treatment were examined by the application of a dye adsorption method which is used widely in the field of histochemistry. The dye adsorption of corona-treated sample was carried out after being evacuated and purged with nitrogen to remove ozone and other attached substances to it.

To detect acidic sites, methylene blue (CI-52015) and methylene violet (CI-50205) were used. In the methylene blue method, the specimen was treated with a methylene blue solution buffered to pH 8 with diethyl barbituric acid according to the Tappi standards.[9] In the case of the methylene violet method, the specimen was treated in the various concentration of methylene violet in 0.01 N NaOH. The amount of the adsorbed dye was determined from

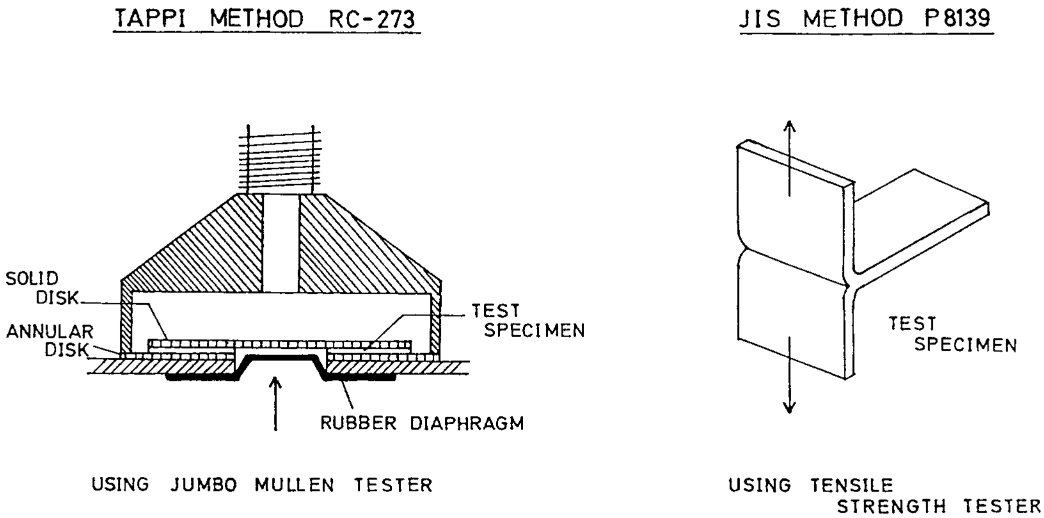

Figure 2 Measurement of plybond strength.

the changes in the concentration of the dye before and after adsorption by spectrophotometry at 620 nm for methylene blue solutions and 550 nm for methylene violet solutions.

Schiff's reagent was used for detecting the presence of aldehyde groups. Schiff's reagent and sulfurous acid rinse solution were prepared by the method described by Lison.[10] The specimen was treated in this reagent for 30 min, rinsed in two changes of sulfurous acid wash, and then washed with water. In order to determine the amount of Schiff's reagent adsorbed, the nitrogen content of the pulp dyed with the reagent which contains nitrogen in the molecule of fuchsin basic (CI-42500) was determined colorimetrically[11] by Kjeldahl degradation of the dyed pulp, followed by indophenol color reaction.

RESULTS AND DISCUSSIONS

Plybond Strength

The effect of the degree of treatment in the corona discharge on the plybond strength of papers measured by the Tappi method is shown in Figure 3. The controls were measured in the same way except that the corona treatment was omitted. The results show clearly a considerable increase in the plybond strength produced by the corona treatment. For both the softwood and hardwood BKP, it is noted that the plybond strength is about twofold higher for the corona-treated pulps than for the untreated controls.

Figure 4 shows the plybond strength measured by means of the JIS method. In this case, the bonding effect for the softwood BKP was also remarkable with an increase in the degree of treatment. However, the bond strength for the hardwood BKP increased rapidly in the initial mild treatment, and then gradually decreased. This may be due to an excessive degrading of the pulp surfaces.

The moisture content of the wet pulp sheet when undergoing corona treatment seemed to have some effect on the plybond strength produced. This is shown in Figure 5. The optimum for the moisture content of pulp sheets during the corona treatment was about 70%.

Water Absorptiveness and Moisture Regain

As shown in Figure 6, the water absorption of the plybonded paper made from the corona-treated pulp

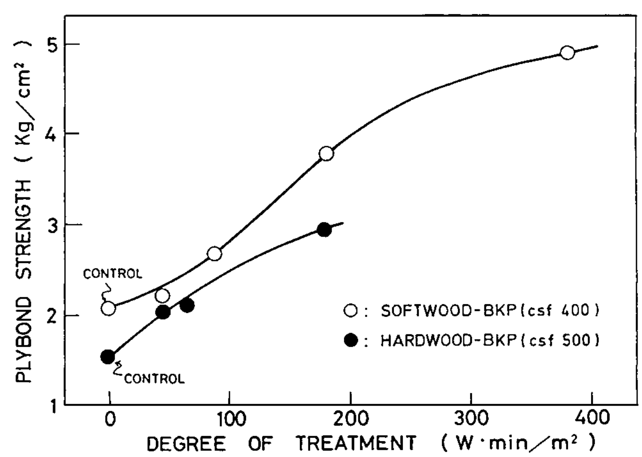

Figure 3 Variation of plybond strength with degree of treatment (tested by the Tappi method).

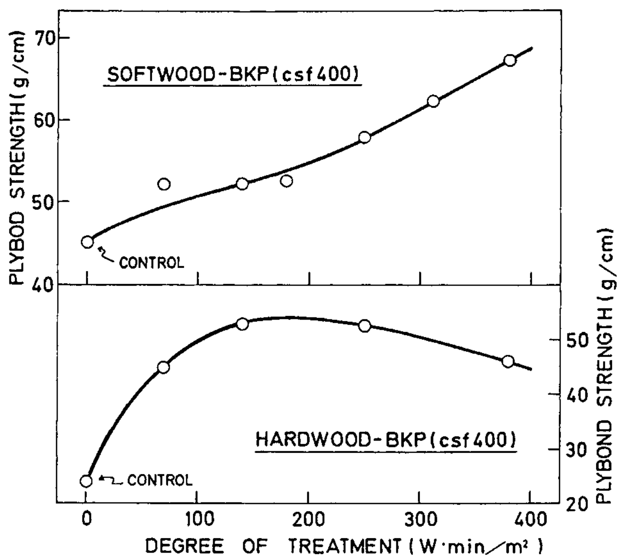

Figure 4 Variation of plybond strength with degree of treatment (tested by the JIS method).

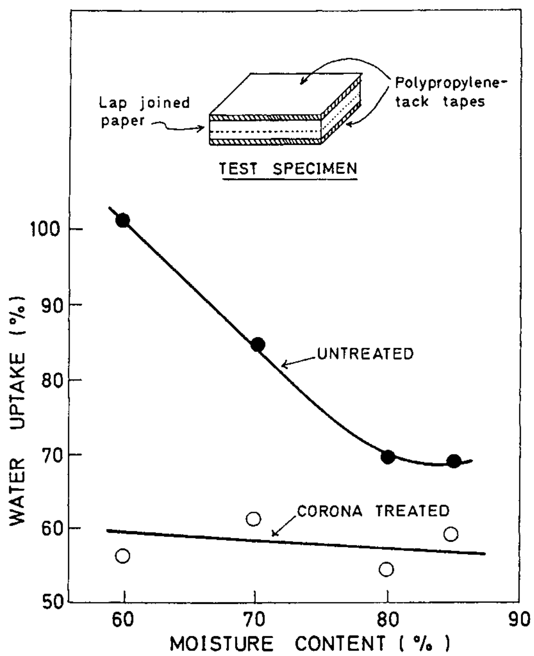

Figure 6 Water absorptiveness of paper vs. moisture content of pulp sheets during corona treatment (softwood-BKP, moisture content of pulp sheets at lap joining: 85%).

sheets was lower than that of the untreated controls. The corona treatment seems to produce strong joints, which will tend to depress the penetration of water into the paper.

Figure 7 indicated that the corona treatment decreased the moisture absorption of the pulps. Contrary to this moisture absorption process, when the wet pulp specimens were immediately subjected to the moisture desorption process, the moisture content of the corona-treated specimens was comparable to that of the corresponding controls.

Above results suggest that a certain change occurs on the treated pulp surface during the drying process after corona treatment. This will be discussed later.

Dye Adsorption

From the above-mentioned experiments, it can be pointed out that the treatment of pulp surface in

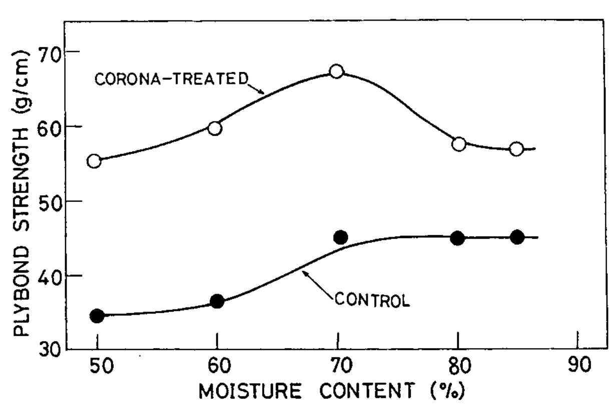

Figure 5 Effect of moisture content of pulp sheets during corona treatment on plybond strength (softwood-BKP, csf 400, treatment: 380 W min/m^2).

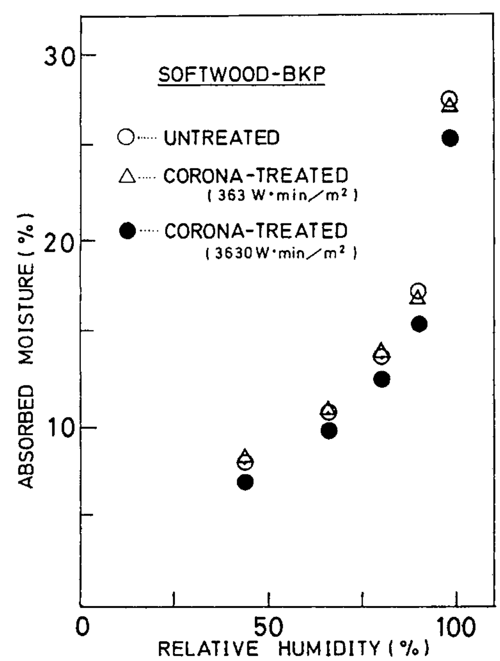

Figure 7 Moisture regain of untreated and corona-treated pulps (sample: vacuum-dried pulp).

corona can cause a considerable increase in the bondability of the surface. In connection with the cause of a remarkable effect observed in this work, some experiments were then carried out in order to elucidate the nature of any chemical changes occurring on the pulp surface.

It is important to note that the chemical changes will be restricted to the surface and does not appear to affect the bulk properties of the pulp. Therefore, in this work, the chemical effects of the corona treatment were examined by the application of a dye adsorption method which is used widely in the field of histochemistry.

In the dye adsorption experiments, a very thin pulp sheet, such as tissue paper, was used for the corona treatment in order to have a large surface area available. The basis weight of the pulp sheet was 6 g/m^2 in this case.

At first, the changes in the functional groups were examined in order to clarify the extent of oxidation, if any, of pulp during the corona treatment. If the corona treatment increases carboxyl groups in pulp, the treated pulp should show an increase in the adsorption ability for basic dyes such as methylene violet and methylene blue. Both the untreated control and the corona-treated pulps adsorbed methylene violet in the same extent of coloration. The dyeing with methylene blue also showed the similar result.

For a more detailed analysis of the dyeing ability of the pulp, the dye adsorption isotherms were measured. The results are shown in Figure 8. The adsorption isotherm for the corona-treated pulp agreed very closely with that for the untreated, and gave a single straight line in the both cases of the hardwood- and the softwood-BKP.

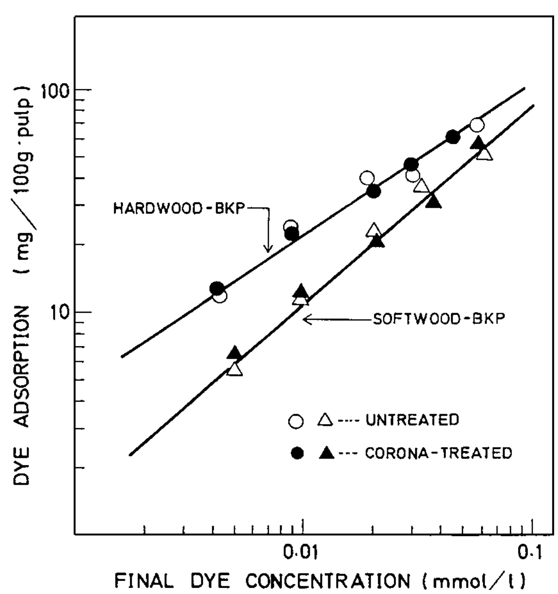

Figure 8 Adsorption isotherms of methylene violet (corona treatment: 3630 W min/m^2).

Table I Carboxyl Groups Content of Pulps Determined by the Methylene Blue Method

Sample	Degree of Corona Treatment (W min/m^2)	Carboxyl Content (mmol/100 g pulp)
Softwood-BKP	Untreated	3.19
	363	3.31
	3630	3.10
Hardwood-BKP	Untreated	4.35
	168	4.07
	1815	4.08

The determination of carboxyl groups in the pulps was carried out by the methylene blue method according to Tappi standards T 237. This is shown in Table I. This result also indicated that no differences in the carboxyl content were observed between the corona-treated and untreated pulps.

From the above dye adsorption experiments, it is clear that no measurable acidic sites such as carboxyl groups increased on the pulp during the corona treatment.

To detect aldehyde groups, the dyeing examination of pulp with Schiff's reagent was made. It is well known that ordinary aliphatic aldehyde groups with Schiff's reagent develop a lasting red ~ violet color.

The corona-treated pulps adsorbed the Schiff's reagent, and the extent of coloring changed with the corona treatment. The results clearly showed a higher dyeing ability for the corona-treated pulps compared with the untreated, indicating that aldehyde groups increased with an increase in the degree of corona treatment.

The nitrogen content of the pulp dyed with Schiff's reagent is shown in Figure 9. This is based on the presence of nitrogen in Schiff's reagent. The amount of nitrogen in the dyed pulp increased with the degree of corona treatment. This means that aldehyde groups, oxidized groups, increased during the corona treatment.

Incidentally, by the corona treatment in nitrogen both the methylene blue and Schiff's reagent adsorptivities of the pulp were scarcely increased.

From the above dye adsorption studies, it is interesting to note that when the pulp was corona-treated, the oxidation of the pulp surfaces resulted in the formation of aldehyde groups and carboxyl

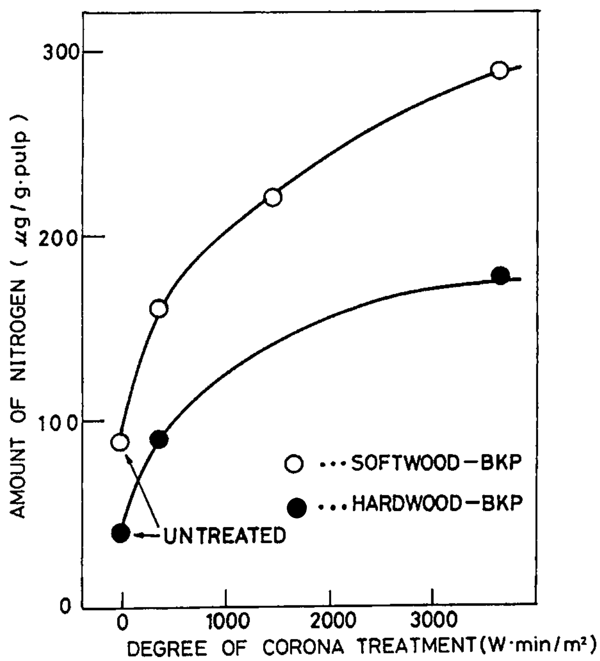

Figure 9 Effect of corona treatment on the amount of nitrogen in the pulps dyed with Schiff's reagent.

groups were not produced. Previously, Goring[1,5] has shown that the corona treatment oxidizes a cellulose film surface to produce carboxyl groups on it. This is in contrast to the result of the present work. This may be due to an excessive oxidation in Goring's work, in which a much longer time of treatment, that is, 4 h, was used.

CONCLUSION

The present work has shown that the treatment of the surfaces of wet pulp sheet in a corona discharge can cause a considerable increase in the bonding properties of the surface.

The use of a corona discharge to increase surface bonding is not new. To increase the adhesion of extrusion coating onto paper and the printability of polyolefin films, corona treatment has been used widely. However, the present work is the first demonstration of the application of a corona discharge to wet state of pulp sheet. What is the cause of the remarkable effect?

From the above-mentioned results, one possibility is that the bonding is related in some manner to the formation of aldehyde groups on the surfaces of the pulp sheet. The reaction of cellulosic hydroxyls with aldehyde to produce hemiacetals or acetals is well known. If this occurs intermolecularly, the cellulose is crosslinked.

Consequently, it is considered possible that the observed corona-induced plybonding of pulp sheet is due to the such interfiber crosslinking, perhaps forming hemiacetals.

A further possibility is that the improved bonding is due to degradation of the pulp surfaces by the corona treatment. With respect to this problem, we have found that hemicellulose isolated from a hardwood produce a product of low molecular weight at lower levels of corona treatment.[12]

It is possible that such a degraded product will act as a glue in sticking the surface together.

This work is now in progress, and further work is required in order to show clearly the effect of chain scission of polysaccharides on the bonding properties of pulp.

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