Transactions of the Materials Research Society of Japan. Vol. 20

Effect of corona discharge treatment on acetylation of cellulose

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A corona pretreated filter paper pulp was acetylated in vapor phase to improve the wet strength of the paper.

Acetyl content was increased with an increase in degree of corona discharge treatment and a maximum was obtained with degree of corona treatment in 10.27 kW·min/m^2. A wet tensile strength showed same tendency. Dry tensile strength and folding endurance showed maximum in different degree of corona discharge treatment in 1.28 kW·min/m^2.

As a result of a chain scission of cellulose molecules and an increase in specific surface area of filter paper pulps by corona discharge treatment, an acetylation reaction was accelerated. In this corona discharge treatment, under conditions of same irradiation, a low current treatment have given excellent results in dry and wet tensile strength.

1. INTRODUCTION

Paper boards, such as news papers, magazines and corrugates, are recovered ca. 87 % in Japan. But, wrapping papers are recovered little, because of an increase in use of waterproof processed papers. They are made form paraffin, synthetic polymers, and pulps. It is difficult to separate these processed papers into elements when discarded.

Corona discharge is used for the surface activation of synthetic polymers and woods. [1-3] For example, hydrophobic synthetic polymer film is treated by corona discharge before printing, gluing or laminating. Recently, it has been researched in the fields of medical and electronic materials. [4]

Acetylation is used for the improvement of water resistance, white stability, anti-deterioration, or electric insulation of woods. [5] It seemed that vapor phase acetylation to acetylate a part of noncrystalline region of cellulose is best for a preparation of waterproof paper. Corona discharge affected the surface region of 1-100 nm. [6]

In this study, effects of corona discharge on acetylation and on physical and chemical properties of paper were examined. Waterproof papers produced by this method are biodigestible even if they are discarded. Further, they are deacetylated with dipping in a dilute alkaline solution. Cellulose fibrils are able to be used in regenerated papers.

2. EXPERIMENTAL

2.1 Materials and corona treatment

Chromatography paper (ADVANTEC No. 51B) was used and its size was 20 cm (machine direction) × 10 cm.

A conventional covered roll corona treater (Kasuga Denki Co. Ltd., HFSS-101) was used. The applied potential was 34 kV_{p-p}, with a frequency of 30 kHz. The air gap between electrodes was 3.0 mm, and line speed was 16.63 m/min. Primary current in the high frequency generator was 4A, and primary voltage was 200 V (DC). Degree of treatment was 0.321 kW·min/m^2 per one pass.

2.2 Acetylation

Papers were acetylated within 12-48 hours after the corona treatment. The corona-pretreated paper was acetylated in a 3 L vessel at 140℃ with acetic anhydride. After the acetylation, the paper was rinsed with tap water and distilled water, and was air dried.

Acetyl content was determined by alkali saponification. [7] About 1g of oven-dried sample was added into mixture of 10 ml of 75% ethanol and 25 ml of 0.5 N sodium hydroxide aq. at 25℃. After 24 hours stirring, the solution was titrated with 0.5 N sulfuric acid aq.

2.3 Tensile strength and folding endurance of paper

Dry tensile strength was determined by JIS P8113 (Testing Method for Tensile Strength of Paper and Paperboard), a span was 100 mm. Wet tensile strength was determined by JIS P8135 (Testing Method of Wet Tensile Breaking Strength of Paper and Paperboard).

Folding endurance was determined by JIS P8115 (Testing Method for Folding Endurance of Paper and Paperboard by MIT Tester) under 0.5 kgf tension.

2.4 α, β, γ -cellulose, specific surface area and freeness

Composition of cellulose was determined by JIS P8101 (Testing Method for Dissolving Pulp).

Specific surface area of paper was determined by BET nitrogen adsorption method [8,9] with Quantasorb Jr. (Yuasa Ionics Co. Ltd.).

Freeness was determined by JIS P8121 (Testing Method for Freeness of Pulp). A 5 g of dry paper was beaten with 1 L of water at 300 rpm. for 2.5 min.

3. RESULTS AND DISCUSSIONS

3.1 Effect of corona discharge

3.1.1 Degree of acetylation

Effect of corona discharge treatment on acetylation of cellulose is shown in Fig. 1. Cellulose samples were acetylated 1 or 3 hours. Acetyl content increased at early stages of treatment, and showed a maximum at 10-20 kW·min/m^2. The maximum acetyl content of 3 hours corona treated cellulose was twice that of 1 hour corona treated cellulose. Degree of substitution (DS) was 0.057 for the maximum of 3 hours corona treated cellulose.

There is a marked decrease in acetyl content for longer treatment times. This decrease for 3 hours acetylation was larger than that for 1 hour acetylation, because of the eluation of acetylated corona pretreated layer from corona treated cellulose by washing. [10,11] This eluation was confirmed by another experiment.

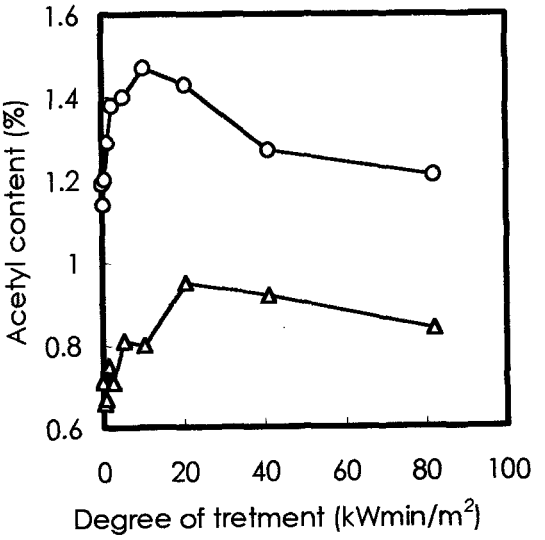

Fig. 1 Effect of degree of corona discharge treatment on acetyl content.
—△—: 1h acetylation
—○—: 3h acetylation

3.1.2 Tensile strength and folding endurance

Effect of corona discharge treatment on wet tensile strength of acetylated cellulose paper is shown in Fig. 2. Since the tendency of this wet tensile strength is as same as that of the acetyl content in Fig. 1, the acetylation must be the cause of improvement of the wet strength. The wet strength of maximal improvement (60 %)

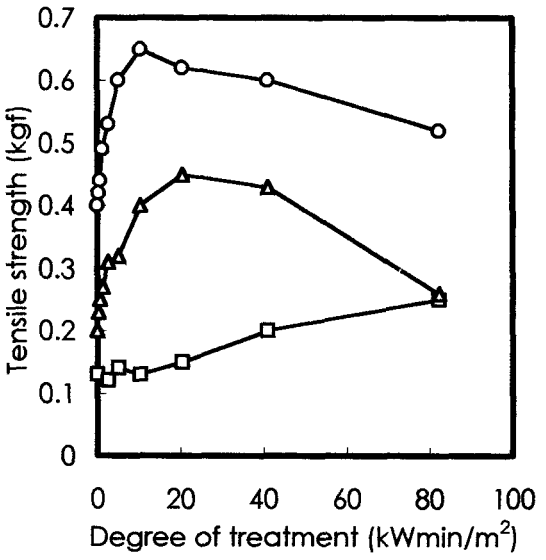

Fig. 2 Effect of corona discharge treatment on wet tensile strength.

—□—: no acetylation
—△—: 1h acetylation
—○—: 3h acetylation

was obtained with DS 0.057.

The zero span strength did not change by corona treatment, [12] and the change in crystallinity of cellulose calculated from density, water adsorption and X-ray diffractogram was little. [13] Holes of 10-20 μ m ϕ formed by corona treatment on pulps, and a diameter of these holes increased by SEM observation. Therefore the strength of the paper degraded for longer treatment times by the corona.

Dry tensile strength increased at an early stage of treatment for both 1 and 3 hours acetylation. However, there is a marked decrease in dry tensile strength for longer treatment times by the corona. The maximum dry tensile strength was obtained at different degree of treatment from the acetyl content or wet tensile strength. Interfibril hydrogen bonds cleaved by introducing of acetyl groups to fibrils. [14,15]

Folding endurance has the same tendency as the dry tensile strength, and was 1 above the corona treatment in 20.54 kW·min/m² for 3 hours acetylation.

3.1.3 Composition of cellulose

Changes in α , β and γ -cellulose composition by the corona is shown in Fig. 3. The α-cellulose content decreased and the β-cellulose content increased with an increase in degree of corona treatment up to 16.05 kW·min/m². The chain scission of α-cellulose occurred by the corona, therefore β-cellulose formed. As compared to Fig. 1, the formation of β-cellulose was related to the increase in the acetyl content. The γ-cellulose content was little. It seemed that γ-cellulose branched to the α and β-cellulose, and did not remain fragments alone.

Shopper-Riegler freeness was measured for corona treated cellulose pulp, to clarify the effect of corona discharge on cellulose fibrils.

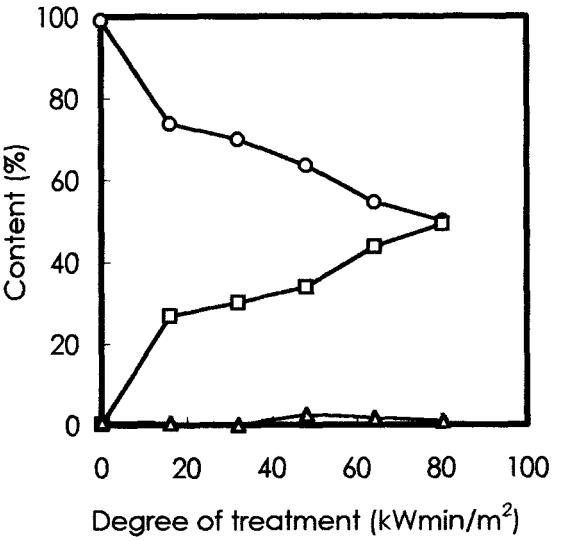

Fig. 3 Effect of corona discharge treatment on α, β, γ cellulose content.

—○—: α-cellulose
—□—: β-cellulose
—△—: γ-cellulose

The freeness was constant up to 16.05 kW·min/m² treatment, and then decreased. As like the result of β -cellulose, the freeness decreased with the decrease in the molecular weight of the cellulose by corona treatment.

Since surfaces of polymer films coarsened by corona treatment, [11,16] the surfaces of corona treated cellulose pulp may be coarsened. Specific surface area of cellulose pulp paper is one of principal element of chemical reaction such as acetylation. Specific surface area of paper was estimated by BET nitrogen adsorption method. The specific surface area increased linearly with an increase in degree of corona treatment from 3.88 m²/g in no corona to 6.28 m²/g in 64.2 kW·min/m².

3.2 Acetylation time

Effect of acetylation time was tested. Levels of corona discharge treatment were 0, 10.27 and 82.18 kW·min/m², no corona, adequate and excess respectively.

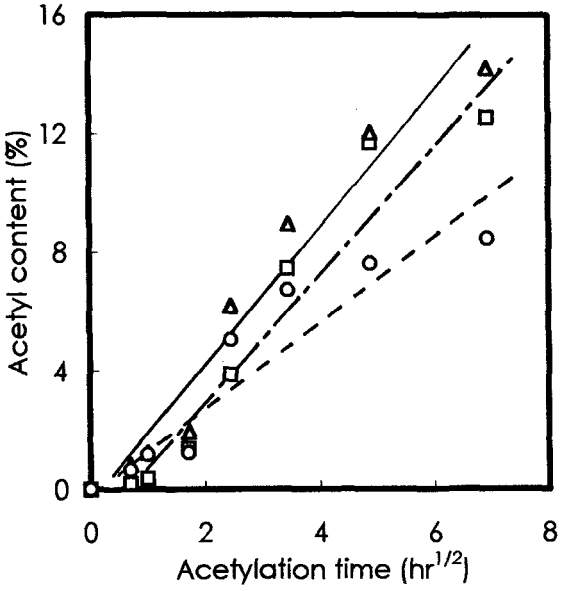

Fig. 4 Effect of corona discharge treatment on acetylation rate.

□ : no corona
△ : 10.27 kWmin/m²
○ : 82.18 kWmin/m²

3.2.1 Acetyl content

The acetyl content was proportional to square root of acetylation time as shown in Fig. 4. The slope as the reaction rate was 2.40 for 10.27 kW·min/m² treatment, and that for 82.18 kW·min/m² treatment was 1.51 which was smaller than that for non corona treatment.

It seems that acetyl content increased with an increase in degree of corona treatment because of an increase in specific surface area and of a decrease in molecular weight. But, acetyl content did not increase by the elution of treated fragments.

This tendency was also seen in Fig. 1, that there is a marked decrease in acetyl content for longer treatment times.

3.2.2 Tensile strength

Effect of acetylation on the wet tensile strength of corona pretreated cellulose pulp paper is shown in Fig. 5. For the optimum

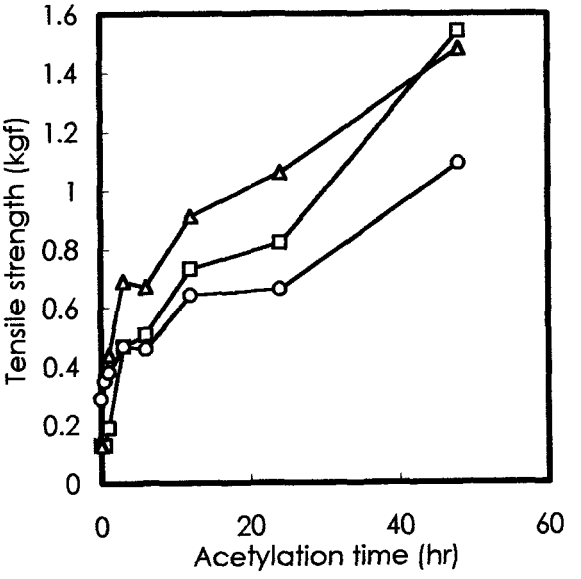

Fig. 5 Effect of acetylation on wet tensile strength.

—□— : no corona
—△— : 10.27 kWmin/m²
—○— : 82.18 kWmin/m²

degree of corona treatment in 10.27 kW · min/m², the wet tensile strength was twice as that of the no corona treated one at an early stage of acetylation. For an excess corona treated cellulose pulp paper, the improvement of the wet tensile strength was little.

Dry tensile strength increased, and a maximal at a corona treatment was in 1.28 kW · min/m². Science, a pulp swells and entanglement of fibrils increases by 4 % of acetylation, a pulp sheet strength increases with an increase in a binding areas of cellulose fibrils. [17] In this experiment, acetyl content attained 4 % by 6 hours acetylation. However, dry tensile strength began to increase at 12 hours acetylation. Binding strength between fibrils began to decrease in 20 % of acetylation. [17] Acetyl content did not attain 20 % by 48 hours acetylation in this experiment.

Folding endurance decreased with an increase in acetyl content.

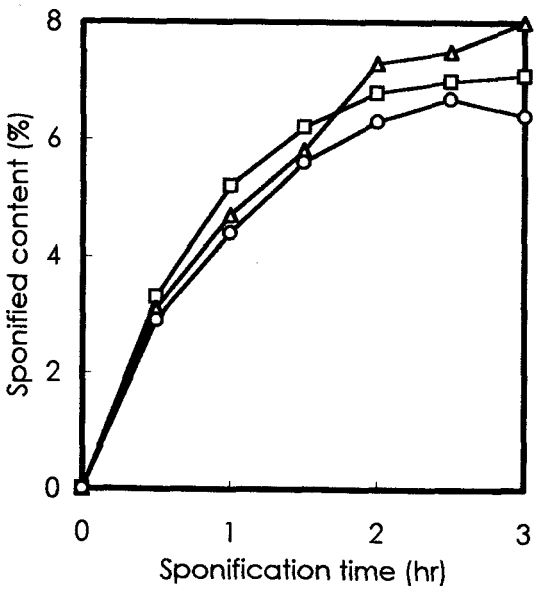

Fig. 6 Effect of corona discharge treatment on saponification of acetylated paper.
—□—: no corona
—△—: 10.27 kWmin/m²
—○—: 82.18 kWmin/m²

3.3 Saponification

Slightly acetylated papers are able to recover as the cellulose papers by saponification. Saponification of corona pretreated acetylated cellulose pulp paper with 0.0625 N NaOH aq. was shown in Fig. 6.

The saponification rate of no corona cellulose was faster than that of corona treated cellulose.

Reaction rate of hydroxyl group at C-6 position in glucose ring is as fast as 5 times more than the hydroxyl groups at the other positions. [17,18] Acetyl groups at C-6 are deacetylated most slowly. [19] But, primary hydroxyl groups are deacetylated faster in dilute alkaline condition as 0.0625 N. [17] In spite of the specific surface area of corona treated cellulose paper increased, the saponification rate decreased. Then it considered that the saponification rate decreased as increase in the steric hindrance surrounding hydroxyl groups by the corona discharge treatment.

3.4 Irradiation rate

An improvement of the wet tensile strength of cellulose pulp paper was achieved by the acetylation and the corona pretreatment in 10.27 kW·min/m². But ca. 30 % of α-cellulose decreased. This is improper for recycling of cellulose pulp paper.

A primary current in the high frequency generator was varied form 1 to 4 A, to control the irradiation rate of corona treatment. Path times were controlled to adjust the degree of corona treatment. Line speed was fixed to 16.63 m/min.

Effect of primary current on acetyl content of cellulose is shown in Fig. 7 and on wet tensile strength is shown in Fig. 8. Both acetyl content and wet tensile strength decreased with an increase in the current. Effect of primary current on the composition of cellulose is shown in Fig. 9. The chain scission of cellulose molecule was a little in low current treatment. A paper corona treated in 4 A was colored in yellow by dipping into 17.5 % NaOH aq. However, the paper treated in 1 A was colored little.

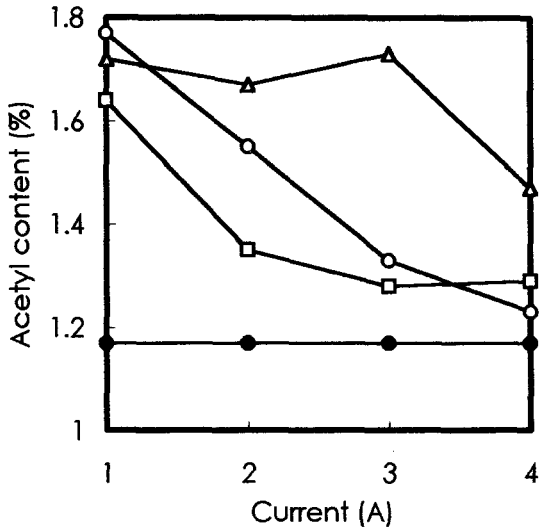

Fig. 7 Effect of irradiation rate on acetyl content.
—●—: no corona
—□—: 1.28 kWmin/m^2
—△—: 10.27 kWmin/m^2
—○—: 82.18 kWmin/m^2

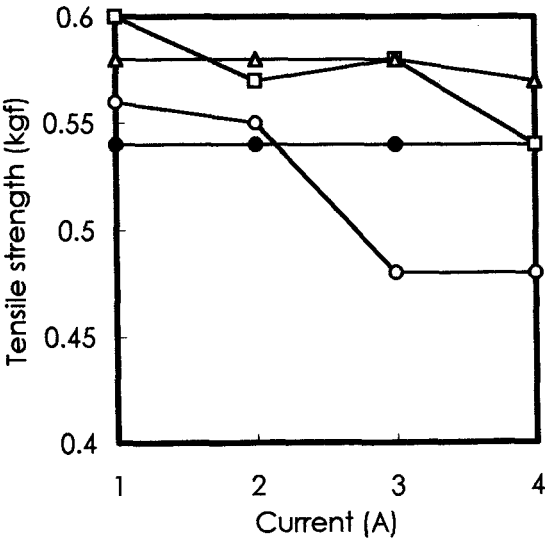

Fig. 8 Effect of irradiation rate on wet tensile strength.
—●—: no corona
—□—: 1.28 kWmin/m^2
—△—: 10.27 kWmin/m^2
—○—: 82.18 kWmin/m^2

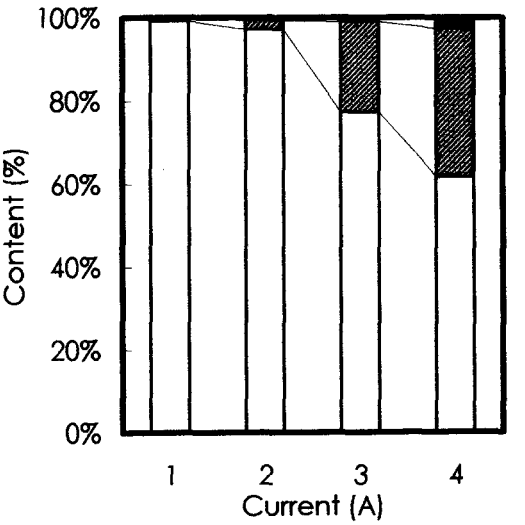

Fig. 9 Effect of irradiation rate on cellulose composition of paper.
16.05 kWmin/m^2
■: γ-cellulose
▨: β-cellulose
□: α-cellulose

Specific surface area of cellulose pulp paper corona treated in 4A was 4.87 m^2/g, and that of corona treated in 1A was 5.62 m^2/g. It seemed that a high density plasma destroyed the fluffiness of paper and the treated surface was planed. Therefore, low current plasma treatment was effective for improvement of paper properties. It is practical to use multiple bar electrodes.

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