

Surface Modification of Paper by Plasma Polymerization at Atmospheric Pressure

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Dry process is more profitable for sizing of paper than wet process because of the needlessness of post-treatments of wasted water and the reduction of environmental stresses. So, in this study a surface sizing by dry process was attempted. Plasma polymerization with ethylene at atmospheric pressure was tested. An electric source was 9 – 15 kV (60 Hz). Gas flow rate was 0.1 – 1.0 L/min. Polyethylene formed on paper surfaces by this treatment. The degree of Stöckigt sizing of filter papers was improved to that of PPC papers. The Penning's effect with carbon dioxide was found out. As color change by this treatment was little, humans' eyes cannot distinguish this treatment.

Key words: plasma polymerization, atmospheric pressure, surface sizing, Penning's effect.

1. INTRODUCTION

Starch, rosin, alkyl ketene dimmer, alkenyl succinic anhydride and synthetic polymers have been added to pulp slurry (internal sizing) or spread (surface sizing) on pulp sheets to control permeability of liquids into papers. Because mechanisms of sizing have not been clarified, sizing of papers has been carried in traditional wet process. Therefore recovery of wasted water and great energy consumption for drying process have been problems.

In this study, the surface sizing in a dry process was done by plasma polymerization with ethylene at atmospheric pressure.

2. EXPERIMENTAL

2.1 Samples and plasma treatment

Cellophane removed softening agents and a filter paper (ADVANTEC 51B) were conditioned at 20°C and 76%RH. Parallel plate electrodes consisted of stainless steel plates (130 X 70 mm) were covered by two glass plates (170 X 110 mm) respectively to prevent electric arc discharge (Fig. 1). The distance between electrodes was 5.5 mm. Samples were discharged up to 15 kV (60 Hz).¹⁾ Pure ethylene gas (99.9%, Nippon Sanso Co.) diluted with carbon dioxide or nitrogen was led into this apparatus.

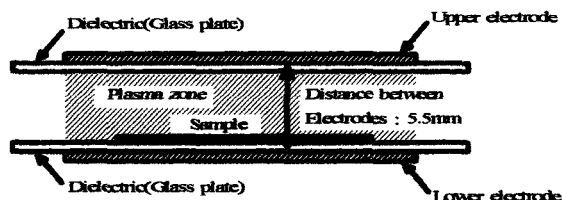


Fig. 1 A schematic representation of electrodes.

2.2 Contact angle and surface-free energy of solid

The contact angle with glycerine and diiodmethane was measured after 24 hours from discharging. Surface-free energies of treated samples were calculated from contact angle data with these two

liquids by geometric mean method.²⁾

2.3 Infrared spectrum

Infrared spectra were taken with a JASCO model FT/IR-620 by using ATR method.

2.4 Degree of Stöckigt sizing

Degree of sizing was determined by JIS P 8112. Plasma treatment was carried out for double sides of papers in this sizing test. The first treated side was contacted to a 2% ammonium thiocyanate solution.

2.5 Color difference

Color of samples was measured by a color meter (Minolta CR-3700d). Conditions were D-65 and 10-degree field. L* a* b* system (CIE 1976) was used for color specification.

3. RESULTS AND DISCUSSION

3.1 Surface-free energy of solid

As paper is porous material, its sizing property is affected by its own wettability, permeability and

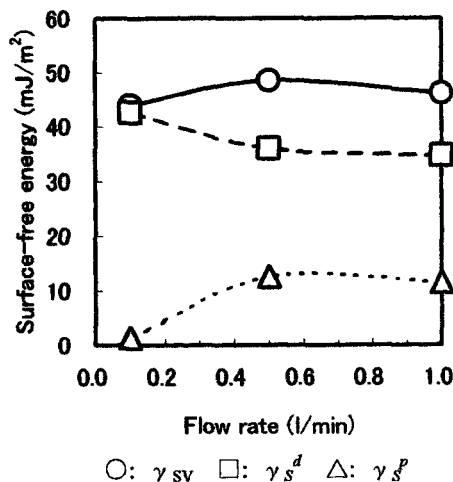


Fig. 2 Effect of gas flow rate on surface-free energy of plasma treated cellophane.

Discharging conditions: 100 % ethylene, 12 kV, 300sec

swelling property. In this study, the wettability of the sample surface was evaluated by the surface-free energy that was calculated from contact angle data.

Effect of the gas flow rate on the surface-free energy is shown in Fig. 2. The contact angle with glycerin was maximum at 0.1 L/min, and polar component in surface-free energy of solid (γ_s^p) decreased to zero drastically. The surface-free energy of solid (γ_{sv}) also decreased. Unfortunately gas flow rate 0.1 L/min was lowest setting for the apparatus.

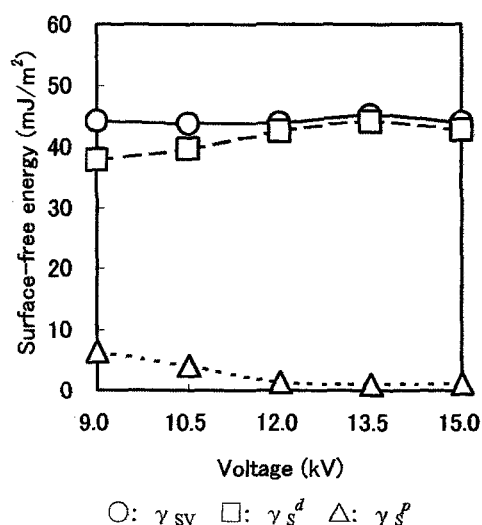


Fig. 3 Effect of discharging voltage on surface-free energy of plasma treated cellophane.

Discharging conditions: 100% ethylene, 300 sec, 0.1 L/min

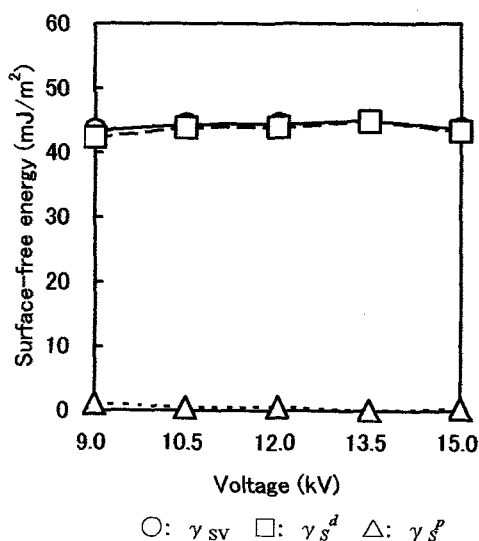


Fig. 4 Effect of discharging voltage on surface-free energy of the cellophane plasma treated in carbon dioxide.

Discharging conditions: 50% ethylene, 300 sec, 0.1 L/min

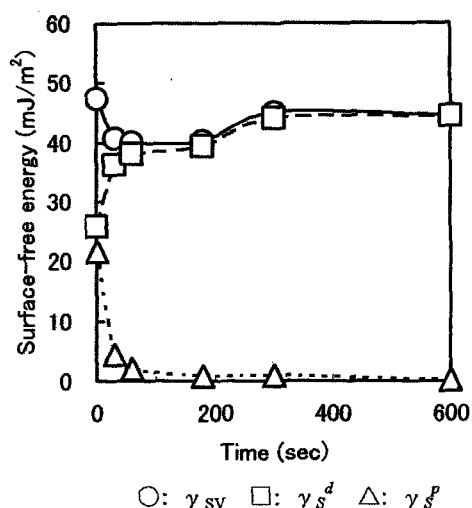


Fig. 5 Effect of discharging time on surface-free energy of plasma treated cellophane.

Discharging conditions: 13.5 kV, 0.1 L/min, 50% ethylene in carbon dioxide

Effect of discharging voltage on the surface-free energy is shown in Fig. 3. The surface-free energy of the treated surface depended on the discharging voltage a little in 100% ethylene. But it did not depend on the discharging voltage in the mixed ethylene with carbon dioxide or nitrogen in this experimental condition of 9.0 to 15.0 kV (Fig. 4).

Effect of the discharging time on the surface-free energy is shown in Fig. 5. The surface-free energy (γ_{sv}) decreased with an increase in discharging time and showed minimum values at 60 to 180 sec in the case of the discharging in ethylene, and γ_{sp} decreased to zero.

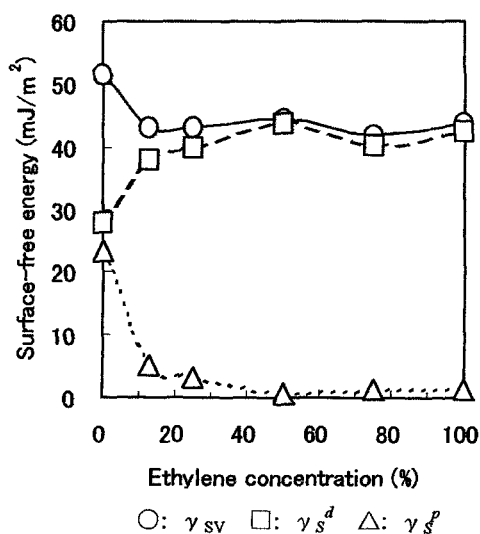


Fig. 6 Effect of ethylene concentration on surface-free energy of the cellophane plasma treated in carbon dioxide.

Discharging conditions: 12 kV, 300 sec.

As shown in Fig. 6, γ_s^p decreased with an increase in ethylene content in carbon dioxide, and showed the minimum value at 50 to 75 % of ethylene. Whereas dispersion component in surface-free energy (γ_s^d) showed the maximum value.

In the case of mixed with nitrogen, the almost same tendency was shown. The value of γ_s^p was zero in 12.5 - 100 % ethylene content in nitrogen.

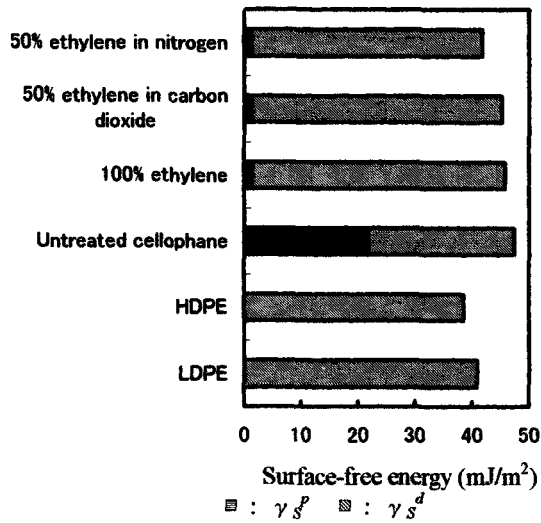


Fig. 7 Surface-free energy of the samples treated in the various conditions.

Discharging conditions: 13.5 kV, 300 sec, 0.1 L/min.

Surface-free energies of the cellophane treated in mixed gases, and of the untreated cellophane, low-density polyethylene and high-density polyethylene are shown in Fig. 7. Most hydrophobic surface was created in the condition of 50% ethylene in carbon dioxide, and γ_s^p was nearly equal to zero. The surface with the lowest surface-free energy was created in the condition of 50% ethylene in nitrogen.

The wettability of cellophane that has a hydrophilic surface decreased and was closer to that of polyethylene by the plasma treatment, and it suggests the deposition of polyethylene.

By the mixing of carbon dioxide or nitrogen, surfaces of cellophane treated with mixed gases are more hydrophobic than that of treated with ethylene only. Therefore activated carbon dioxide (CO_2^*) or nitrogen (N_2^*) transferred their own active energies to ethylene molecules (Penning's effect).⁴⁾

On the other hand, different behavior between the gases mixed with carbon dioxide and nitrogen may be caused by difference of ionization potential of carbon dioxide and nitrogen (13.78 and 15.59 eV, respectively).⁵⁾ Carbon dioxide that is easy to ionize may form some polar groups on the treated surface, reacted with ethylene in gas phase and deposited into polyethylene. So γ_s^p may increase.

3.2 Infrared spectrum

Because of a little change in spectrum between before and after the treatment on cellophane, the

difference spectra were calculated to cancel the absorption bands due to cellophane and to find absorption bands due to polyethylene. The difference spectra are shown in Fig. 8. Big peaks near 2400 cm^{-1} were due to carbon dioxide in air. An absorption band ranging in 2960 to 2850 cm^{-1} that was assigned to polyethylene increased a little in every treated conditions.

Since a spectrum of cellophane was not hidden by a spectrum of the formed polyethylene, the thickness of the deposited polyethylene may be very thin. It may be less than the infrared wavelength. For the sample treated in carbon dioxide, an absorption band at 1715 cm^{-1} increased a little.

These results above mentioned differed from the previous results on the cellophane.⁶⁾ The reason may be due to the effect of the mixed gas.

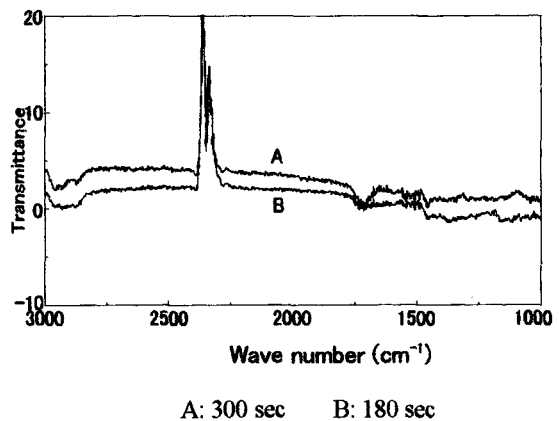


Fig. 8 Difference spectra of cellophane treated with 50 % ethylene in carbon dioxide, at 13.5 kV, 0.1 L/min.

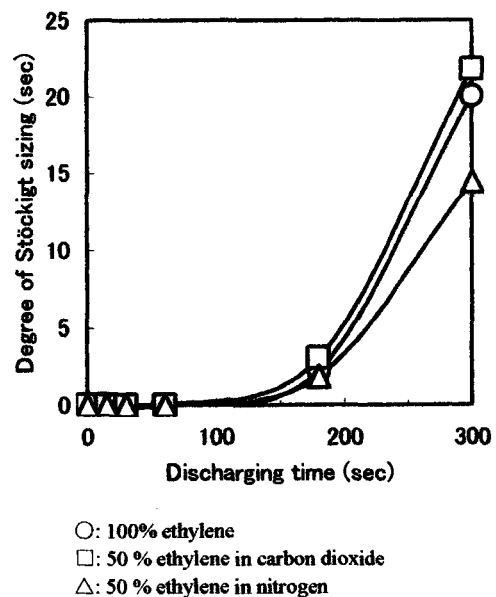


Fig. 9 Effect of discharging time on degree of Stöckigt sizing.

Discharging conditions: 13.5 kV, 0.1 L/min

3.3 Degree of Stöckigt sizing

In the case of the use of filter papers that had not been sized for samples of plasma polymerization, it is hard to evaluate the treated surfaces by the contact angle data, so Stöckigt sizing test was carried out and a result is shown in Fig. 9. Further a comparison data of Stöckigt sizing to a PPC paper is shown in Fig. 10. In this experiment, maximum degree of Stöckigt sizing was 21.8 sec in the case of the mixed gas with carbon dioxide. Secondary value was 20.1 sec in ethylene. Whereas it was 14.4 sec in the case of the mixed gas with nitrogen. Since polyethylene was deposited on treated filter papers from gas phase ethylene, filter papers may be sized by the dry process.

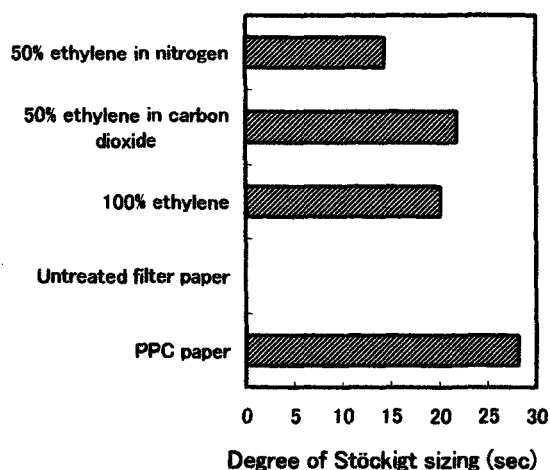


Fig. 10 Degree of Stöckigt sizing for various treated samples.

Discharging conditions: 13.5 kV, 300 sec, 0.1 L/min

3.4 Color difference

Whiteness and hue are important properties of papers as same as basis weight, thickness, glossiness (luster), flatness and gas permeability.

Brightness difference (ΔL^*), ab-chroma difference (ΔC_{ab}^*), ab-hue difference (ΔH_{ab}^*), and color difference (ΔE_{ab}^*) between before and after treatment were calculated. ΔH^* is shown in Fig. 11. All numerical values changed within 0.3 to 1.0. Humans' eyes cannot detect these little change.

4. CONCLUSION

Deposition of the polyethylene from the ethylene on cellophane by plasma polymerization was confirmed by as following results; contact angles with glycerine increased with an increase in the degree of the deposition treatment and the calculated γ_s^p decreased to zero. A shoulder assigned to polyethylene was slightly appeared in FT-IR spectra, the degree of the Stöckigt sizing was improved by this treatment. The best condition in this experiment was the condition of 13.5kV, 300 sec, 50% ethylene in carbon dioxide and 0.1 L/min.

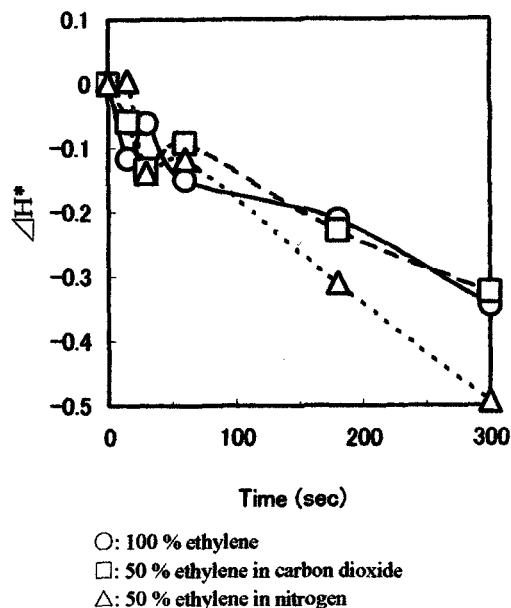


Fig. 11 Effect of discharging time on differential H^* (ΔH^*) of plasma treated filter paper.

Discharging conditions: 13.5 kV, 0.1 L/min

In this paper, filter papers that were not internal sized and had great permeability of liquids, were selected to avoid the effect of internal sizing. So, the maximum degree of Stöckigt sizing was ca. 22 sec. There must be no problem to use internal sized papers for surface sizing by plasma polymerization of ethylene.

Further Penning's effect confirmed the result that polymerization was accelerated by gas mixing. Dilution of ethylene with carbon dioxide must contribute to avoid explosion or combustion of ethylene in processing and to reduce the consumption of ethylene.

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