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(Received July 17, 1992)

Analysis of the Functional Groups Formed on the Corona-Treated Cellulose Fibre Sheet Surface by Means of Chemical Modification in Liquid Phase-ESCA Technique**Atsushi Sawatari and Hiroshi Nakamura*

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Abstract: The cellulose sheet surface with various durations of corona treatment were characterized by chemical modification in liquid phase-ESCA technique. Whatman #1 filter paper, regenerated cellulose film, handsheet from thermomechanical pulp (TMP), and handsheet from softwood bleached sulfate pulp (N-BKP) were used after washing with ethanol/benzene mixture. Carboxyl groups were found on the main chain of lignin on the surface of handsheet from TMP. However, no carboxyl groups were found on the main chain of the surface of the other cellulose sheets, namely, Whatman #1 filter paper, regenerated cellulose film and handsheet from N-BKP. Carbonyl groups were introduced on the main chain of the surface of the all sheets used, after the treatment with corona discharge. Chemical modification-ESCA technique was very effective for the analysis of functional groups formed on the cellulose fibre sheet surfaces.

1. Introduction

Corona discharge treatment has been widely used as an essential pretreatment technique of paper web for extrusion coating of molten polyolefins onto the web [1]. However, the surface activation mechanism of paper by this treatment has not been established yet [2,3]. In order to elucidate the chemical changes on the surface of cellulose sheet by this treatment, the corona-treated cellulose sheets were characterized by chemical modification-ESCA technique [4]. ESCA is one of the most useful method for the analysis of polymer surfaces at present, and chemical modification gives chemical selectivity for the functional groups formed on the sample surfaces. Everhart et al. [4] demonstrated that the chemical modification-ESCA technique was very effective method for qualitative analysis of the functional groups on the various po-

lymer surfaces. However, they also pointed out that this technique was not always appropriate for quantitative analysis. One of the authors discussed the relationship between the relative intensities F_{1s}/C_{1s} obtained by this technique and the carbonyl groups content of the powder prepared by pulverizing Whatman #1 filter paper oxidized by periodate [5]. The relative intensities F_{1s}/C_{1s} were found to be almost linearly related to the carbonyl content. The authors demonstrated originally by using chemical modification-ESCA technique that corona-treated cellulose sheet surface has carbonyl groups [6].

In this study, the formation of carboxyl group on the surface of cellulose sheets were examined by using chemical modification with trifluoroethanol and Ca^{2+} ion in liquid phase. A comparison was made between introduction of carboxyl and carbonyl groups by the corona discharge treatment.

2. Experimental

Fig. 1 shows experimental sequence adopted in this experiment. All sheets were extracted with ethanol/benzene mixture, since surface deposition of carbon rich extractives occur on the pulp fibres under ordinary conditions [7,12,14]. Four types of cellulose

* The main part of this report was presented at "Cellucon 90" held at Bratislava in Aug. 1990.

この報文を「コロナ処理済セルロース繊維シート表面の化学修飾-ESCA法による研究(第1報), Surface Characterization of the Corona-Treated Cellulose Fibre Sheet by Chemical Modification-ESCA Technique (Part 1)」とする。

Fig. 1 Experimental Sequences

Fig. 2 Derivatization Reaction.

sheets were treated with corona discharge in O₂ atmosphere, chemically modified, and their surfaces were characterized by ESCA. Three kinds of derivatives were used for ESCA measurement as shown in Fig. 2. If the sample surface possesses carboxyl groups, the groups react with trifluoroethanol (TFE) to give trifluoroethylester. Carboxyl groups also react with Ca²⁺ ion to give calcium carboxylate. After derivatization, F_{1S} peak or Ca_{2P} peak were observed in ESCA spectra. If the sample surface has carbonyl groups, they react with pentafluorophenylhydrazine (PFPH) giving pentafluorophenylhydrazone, and then F_{1S} peak should appear in ESCA spectra.

2.1 Sample Sheets

Four types of the cellulose sheets were prepared for the following experiments. Radiata pine TMP was beaten to 170 mL C.s.f. by Valley beater, and the handsheets were made from beaten TMP. Handsheets were also made from N-BKP beaten by PFI mill to 400 mL C.s.f. Handsheet from TMP, handsheet from N-BKP and Whatman #1 filter paper were Soxhlet extracted with ethanol/benzene mixture for 10 h. After the extraction treatment, the sample sheets were air-dried. Commercially available cellophane was im-

mersed in a stream of tap water over night. The tap water-washed cellophane was washed with distilled water and organic solvents, and dried while applying a tension in the atmosphere of 20 °C and 65% RH. The air-dried sheets and films were stored in a silica gel containing desiccator.

2.2 Corona Discharge Treatment

A batch type discharging equipment [8] was used in this experiment. Discharging conditions were as follows: discharging voltage 13 kV, discharging frequency 50 Hz, discharging power 4.01 watts, discharging period 0 ~ 3600 sec, electrode size 100 mm × 100 mm × 5 mm, atmosphere O₂ gas flow of 80 mL/min, gap between the electrodes 5.2 mm, thickness of dielectrics (glass plate) 2.9 mm, air gap 2.2 mm, temperature 20 °C and pressure atmospheric pressure.

2.3 Chemical Modification (Derivatization)

Derivatizations were carried out by the following procedures. Corona-treated sheet samples were reacted with three kinds of reagents, respectively.

2.3.1 Derivatization with TFE

1 mL of TFE was added in the mixture of 2 mL pyridine, 400 mg of dicyclohexylcarbodiimide (DCC) and 30 mL of dichloromethane. The sample sheets were immersed in 33 mL of the above-described reagent in 200 mL glass stoppered Erlenmeyer flask kept shaking for 15 h at 20 °C. After washing with anhydrous ether, the treated sample sheets reacted were Soxhlet extracted with anhydrous ether for 12 h. The extracted sample sheets were then dried in air at room temperature and stored in silica gel containing desiccator with brownish color. After vacuum drying at room temperature, the derivatized sample sheets were used for the next ESCA measurement.

2.3.2 Derivatization with Ca²⁺ Ion

0.34 mN calcium acetate solution was prepared by diluting 0.5 M calcium acetate to 0.34 mN and pH of the solution was controlled to 6.5 ~ 7.0 by adding appropriate volume of acetic acid and of 0.34 mN calcium hydroxide. The 200 mL glass stoppered Erlenmeyer flask containing corona-treated sample sheets and 100 mL of 0.1 N HCl was kept shaking for 15 min at 20 °C. This procedure was repeated 2 times furthermore and washed with distilled water. And then, the sample sheets were immersed in 100 mL of

the 0.34 mN calcium acetate solution and kept shaking for 15 min. After washing with distilled water, the sample sheets were dried in air.

2.3.3 Derivatization with PFPH

0.1 g of PFPH (Aldrich Chemical Company, Inc.) was dissolved in 100 mL of anhydrous ethanol. Sample sheets were immersed in 50 mL of this solution in 200 mL glass stoppered Erlenmeyer flask and kept shaking for 10 min at 20 °C. After washing with anhydrous benzene and acetone, the reacted sample sheets were dried in air.

2.4 ESCA Measurement

JOEL type JPS-80 was used as a ESCA spectrometer, and JPS-80 Multiground ESX was used to analyse the obtained data. Measuring conditions were as follows: X-ray source $MgK\alpha$ (1253.6 eV), accelerating voltage 10.0 kV, X-ray current 10.0 mA, scanning range 280 - 300 eV for C_{1s} peak, 680 - 700 eV for F_{1s} peak, 340 - 360 eV for Ca_{2p} peak, degree of vacuum 10^{-6} Pa, times of scanning 30 times and without the correction for charge up effect.

3. Results and Discussion

Changes in F_{1s} peak and C_{1s} peak followed by the increase in duration of corona treatment are shown in Fig. 3 for TMP handsheet derivatized with TFE. There are no changes in C_{1s} peak and notable in-

crease in F_{1s} peak intensity with the increase in duration of corona treatment. These results show that carboxyl groups are found on the surface of the corona-treated handsheet from TMP. Two processes may be attributable for the chemical changes on the surface layer of these sample system [7]. One is the formation of some oxygen containing functional groups on the surface layer of frame work or of polymeric main chain of constituent polymers. Another is some scissions or cleavages of polymeric chain. Therefore, compounds with lower molecular weight will be formed on the surface layer of the constituent polymer. As the authors adopted the chemical modification in liquid phase in this study, these compounds with lower molecular weight may be washed out from the surface of the corona-treated cellulose sheet. Therefore, ESCA spectra, which involved in this chemical modification in liquid phase-ESCA technique, are considered to give the information on the main chain residue on the surface layer. Verification of the above assumption will be furthermore discussed in another report [7]. According to the above-described reason, it should be considered that the carboxyl groups are introduced onto the main chain of the surface of TMP handsheet by the corona discharge.

Changes in relative intensity (F_{1s}/C_{1s}), ratio of number of atoms (N_F/N_C) and number of carboxyl groups per total number of carbon atom by the corona treatment were summarized in Table 1 for handsheets from TMP. Ratios of number of atoms (N_F/N_C) were calculated from relative intensities (F_{1s}/C_{1s}) by using Ebel-Hirokawa's method and Physical Electronic's Table concerning atomic sensitivity factor [9-11]. From Table 1, 2.7 carboxyl groups per one thousand of carbon atoms, that is, 2.4 carboxyl per one hundred of C_9 units of lignin were considered to be introduced onto the TMP sheet surface at its maximum.

On the other hand, no F_{1s} peak was observed in ESCA spectra of Whatman #1 filter paper, regenerated cellulose film and N-BKP handsheet (Fig. 4, Fig. 5 and Fig. 6, respectively). This shows that carboxyl groups cannot be detected on the surface of these cellulose sheets by this technique. Accordingly, it may be considered that no carboxyl groups are introduced onto the main chain of the three kinds of cellulose

Fig. 3 Changes in F_{1s} peak and C_{1s} peak of handsheet from TMP by the increase in duration of corona treatment. Derivatization was carried out by using TFE/DCC/Dichloromethane system after corona treatment. TFE: 2,2,2-Trifluoroethanol, DCC: Dicyclohexylcarbodiimide.

Table 1 ESCA Relative Intensity and Number of Carboxyl Groups per Total Carbon Atom for Handsheet from TMP Derivatized with TFE/DCC/dichloromethane System after Corona Treatment

Duration of corona treatment	Area (cps·eV)		Relative intensity ($\times 10^2$)	Atom ratio* ($\times 10^3$)	Carboxyl/C ($\times 10^3$)
	F _{1s}	C _{1s}			
0 sec	37	15600	0.24	0.49	0.16
1 sec	140	16500	0.85	1.74	0.58
3 sec	149	15500	0.96	1.97	0.66
10 sec	165	16300	1.01	2.07	0.69
30 sec	305	15500	1.97	4.03	1.34
100 sec	371	15800	2.35	4.81	1.60
5 min	387	15800	2.45	5.02	1.67
15 min	400	16100	2.48	5.09	1.70
30 min	515	16400	3.14	6.44	2.15
60 min	633	15900	3.98	8.16	2.72

*: Calculated from relative intensity $\times 0.205$. The coefficient 0.205 is quoted from Physical Electronic's Table 5 concerning atomic sensitive factors (ASF).

Fig. 4 Changes in F_{1s} peak and C_{1s} peak of Whatman #1 filter paper by the increase in duration of corona treatment. Derivatization was carried out by using the same method as one in Fig. 3.

Fig. 5 Changes in F_{1s} peak and C_{1s} peak of regenerated cellulose film by the increase in duration of corona treatment. Derivatization was carried out by using the same method as one in Fig. 3.

sheets. In addition, it is interesting in Fig. 5 that spectral intensity of the low binding energy component of C_{1s} peak increases with the increase in duration of corona treatment in the case of regenerated cellulose film. At present, the reason for this phenomenon can not be envisaged clearly. Relative intensities of F_{1s} peak to C_{1s} peak (F_{1s}/C_{1s}) were plotted against the logarithm of duration of corona treatment ($\log t$) as shown in Fig. 7. Fig. 7 shows that the relative intensity (F_{1s}/C_{1s}) increases with the increase in

the duration of corona treatment for TMP handsheet, but any changes in the relative intensities were not found in the other cellulose sheets than the TMP sheet. The TMP handsheet samples have lignin rich surface [12], but Whatman #1 filter paper, regenerated cellulose film and N-BKP handsheet have carbohydrate rich surface [12,13]. Usually the surface layers of these sheets have considerable quantities of extractives, but after extracting with ethanol/benzene

Fig. 6 Changes in F_{1s} peak and C_{1s} peak of handsheet from softwood bleached sulfate pulp (abbreviated as N-BKP hereafter) by the increase in duration of corona treatment. Derivatization was carried out by using the same method as one in Fig. 3.

Fig. 7 Relationship between ESCA relative intensity (F_{1s}/C_{1s}) and logarithm of the duration of corona treatment ($\log t$) for various cellulose fibre sheets which were derivatized with TFE/DCC/Dichloromethane system after corona treatment. $\circ$: TMP handsheet, $\triangle$: Whatman #1 filter paper, $\bullet$: Regenerated cellulose film and $\blacktriangle$: N-BKP handsheet.

mixture, the surface layers of the sheets have almost no extractives [12,14-16]. In this experiment, therefore, all sheet samples were used after extracting with ethanol/benzene mixture or other organic solvents. From Fig. 7, a site of lignin rich surfaces seem

Fig. 8 Changes in Ca_{2p} peak and C_{1s} peak of handsheet from TMP by the increase in duration of corona treatment. Derivatization was carried out by using Ca^{2+} ion after corona treatment.

to be oxidized by the corona discharge to carboxyl groups, but sites of carbohydrate rich surfaces seem to be not oxidized to carboxyl groups. However, strictly speaking, it should be considered that the carboxyl groups are not introduced onto the main chain of the cellulose and hemicellulose on the surface layer of the three kinds of the cellulose sheets, for the above-described reason. It can be thought from Fig. 7 that corona discharge brought about carboxyls on the main chain of the lignin of the TMP handsheets.

Change in Ca_{2p} peak and C_{1s} peak by the increase in duration of corona treatment are shown in Fig. 8 for the handsheet from TMP. There are no changes in C_{1s} peak, but a significant increase in Ca_{2p} peak intensity with the increase in duration of corona treatment. That is, carboxyl groups seem to be introduced onto the surface of the handsheet from TMP.

On the contrary, no Ca_{2p} peaks were found in ESCA spectra of Whatman #1 filter paper, regenerated cellulose film and N-BKP handsheet (Fig. 9, Fig. 10 and Fig. 11, respectively). This shows that carboxyl groups cannot be detected on the surface of these cellulose sheets by using this technique. In addition, it is interesting in Fig. 10 that spectral intensity of the low binding energy component of C_{1s} peak also increases with the increase in the duration of corona treatment in the case of regenerated cellulose film, in a similar manner as in Fig. 5.

Fig. 9 Changes in Ca₂P peak and C₁S peak of Whatman #1 filter paper by the increase in duration of corona treatment. Derivatization was carried out by using Ca²⁺ ion after corona treatment.

Fig. 11 Changes in Ca₂P peak and C₁S peak of hand-sheet from N-BKP by the increase in duration of corona treatment. Derivatization was carried out by using Ca²⁺ ion after corona treatment.

Fig. 10 Changes in Ca₂P peak and C₁S peak of regenerated cellulose film by the increase in duration of corona treatment. Derivatization was carried out by using Ca²⁺ ion after corona treatment.

Relative intensity of Ca₂P peak to C₁S peak (Ca₂P/C₁S) were plotted against the logarithm of duration of corona treatment (log t) as shown in Fig. 12. From Fig. 12, lignin rich surfaces seem to be oxidized by the corona discharge to carboxyl groups, but carbohydrate rich surfaces seem to be not oxidized to carboxyl groups.

Changes in F₁S peak according to the progress of corona treatment shown in Figs. 3 - 7 are consistent with changes in Ca₂P peak in Figs. 8 - 12.

Fig. 12 Relationship between ESCA relative intensity (Ca₂P/C₁S) and logarithm of the duration of corona treatment (log t) for various cellulose fiber sheets which were derivatized with Ca²⁺ ion after corona treatment. Ca₂P peak intensity was calculated from the summation of Ca₂P^{3/2} and Ca₂P^{1/2}; ○: TMP handsheet, △: Whatman #1 filter paper, ●: Regenerated cellulose film and ▲: N-BKP handsheet.

It can be summarized from Figs. 3 - 12 that carboxyl groups were found on the surface of the TMP sheet increasingly according to the progress of corona discharge by this chemical modification in liquid phase-ESCA technique, but no carboxyl groups were found on the surface of the other cellulose sheets than

TMP handsheet by this technique. These results are attributable to the carboxyl formation on the main chain of the lignin rich surface of TMP sheet, and no carboxyl formation on the main chain of the cellulose rich surface of the other sheets.

In addition, it is also interesting that spectral intensity at the low binding energy component of C_{1s} peak increases with the increase in duration of corona treatment in the case of regenerated cellulose film. It may be suggested that the discharge brought about some carbon rich components on the surface of the regenerated cellulose film.

Changes in F_{1s} peak and C_{1s} peak according to the increase in duration of corona discharge treatment are shown in Fig. 13 for TMP handsheet derivatized with PFPH. It can be seen from Fig. 13 that there are no changes in C_{1s} peak and remarkable increase in F_{1s} peak intensity with the increase in the duration. This shows that carbonyl groups can be detected on the surface of TMP handsheet by this technique. Carbonyl groups apparently seems to be introduced onto the surface of handsheet from TMP. Strictly speaking, it should be considered that the carbonyl groups are introduced onto the main chain of the surface of the TMP handsheet by the formerly described reason. Relative intensities of F_{1s} peak to C_{1s} peak (F_{1s}/C_{1s}) were plotted against logarithm of the duration of corona treatment ($\log t$) in Fig. 14. Fig. 14 shows that

Fig. 13 Changes in F_{1s} peak and C_{1s} peak of handsheet from TMP by the increase in duration of corona treatment. Derivatization was carried out by using PFPH/ethanol system after corona treatment. PFPH: Pen-tafluorophenylhydrazine.

the relative intensity (F_{1s}/C_{1s}) increases with the increase in the duration of corona treatment for all sheets used. From Fig. 14, both lignin rich surfaces and carbohydrate rich surfaces seem to be oxidized to carbonyl groups by corona discharge. For the same reason as above-described one, it should be considered that the carbonyl groups are introduced onto the main chain of the surface of all sheets used. The numbers of the introduced carbonyls on the TMP sheet chemically modified with PFPH were calculated by the same method used in Table 1, as shown in Table 2. From Table 1 and 2, large quantities of carbonyl groups were introduced in comparison to carboxyl groups.

It will be a future problem that information about surface concentration of any washable compounds with low molecular weight will be required to understand the state of the corona-treated surface of various cellulose sheets [6,7].

4. Conclusion

About 2.4 carboxyl groups per one hundred of C_9 units of lignin were found on the surface of the corona-treated TMP handsheet at its maximum, while about 10.9 carbonyl groups per one hundred of C_9 units of lignin were found on the surface of the sheet. On

Fig. 14 Relationship between ESCA relative intensity (F_{1s}/C_{1s}) and logarithm of the duration of corona treatment ($\log t$) for various cellulose fiber sheets which were derivatized with PFPH after corona treatment. $\circ$: TMP handsheet, $\triangle$: Whatman #1 filter paper, $\bullet$: Regenerated cellulose film and $\blacktriangle$: N-BKP handsheet.

Table 2 ESCA Relative Intensity and Number of Carbonyl Groups per Total Carbon Atom for Handsheet from TMP Derivatized with PFPH/ethanol System after Corona Treatment

Duration of corona treatment	Area (cps·eV)		Relative intensity ($\times 10^1$)	Atom ratio* ($\times 10^2$)	Carbonyl/C ($\times 10^3$)
	F _{1s}	C _{1s}			
0 sec	870	13,200	0.66	1.35	2.70
1 sec	930	13,200	0.70	1.44	2.89
3 sec	1,510	14,000	1.08	2.21	4.42
10 sec	1,660	13,600	1.22	2.50	5.00
30 sec	2,440	13,600	1.79	3.68	7.36
100 sec	2,530	13,600	1.86	3.81	7.63
5 min	3,290	13,900	2.37	4.85	9.70
15 min	3,470	14,600	2.38	4.87	9.74
30 min	3,340	13,400	2.49	5.11	10.22
60 min	4,010	13,600	2.95	6.04	12.09

* : The atom ratio was calculated by the same method as one in Table 1.

the other hand, no carboxyl groups were found on the surface of other cellulose sheets, while about 6.8 carbonyl groups per one hundred of glucose residues were found on the surface of Whatman #1 filter paper, about 1.5 carbonyls per one hundred of glucose residues on regenerated cellulose film and about 2.1 carbonyl per one hundred of C₅ units of xylose residues on N-BKP handsheet. These values were obtained by assuming that Ebel - Hirokawa's rule [9] holds in the cellulose sheet sample system. However, it is important that the above-described information was originally obtained by adapting this chemical modification in liquid phase - ESCA technique to corona-treated cellulose sheets.

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