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# Surface analysis of paper containing polymer additives by X-ray photoelectron spectroscopy I: Application to paper containing dry strength additives

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**Abstract** The surfaces of handsheets containing polydiallyldimethylammonium chloride (PDADMAC) and anionic polyacrylamide (A-PAM) were analyzed using X-ray photoelectron spectroscopy (XPS). The observed N1s chemical shifts were compared with those of the strength additives. Chemical covalences on paper surfaces due to a small amount of polymer additives were clarified and determined by an XPS curve-fitting technique. Some of the problems associated with surface analysis of paper by XPS are discussed. The effects of strength additives on the fiber surface or between fibers are illustrated. This technique appears promising as a tool to analyze paper surfaces treated with small amounts of polymer additives.

**Key words** XPS · Paper strength additive · Polydiallyldimethylammonium chloride · Anionic polyacrylamide

## Introduction

The surface chemistry of paper plays an important role in the performance of the paper during its end use. When various chemical additives and wood components migrate to the surfaces of fibers, the surface properties of the paper can be changed dramatically. Such additives include, for example, wet-strength resins to improve mechanical strength when the paper is wet[1–3] and sizing agents to impart water repellency.[4–7] Changes in the performance of the paper are strongly related to the functional groups of the additives. Although X-ray photoelectron spectroscopy (XPS) was found to be a powerful tool for chemical analysis of surfaces of synthetic polymers,[8–11] natural and modified textiles,[12,13] and wood and cellulose fibers,[14–25] no detailed study of covalent bonds on the paper surface due to small amounts of polymer additives has been reported in the literature.

We first discuss experimental conditions to confirm by XPS that chemical covalent bonds arise from small amounts of strength additives on the paper surface. As an illustration of the problem-solving capability of this technique, three examples of hand-made paper analysis are described. The first example represents XPS C1s, O1s, and N1s spectra of a hardwood bleached kraft pulp (LBKP) handsheet made with no additive. The second example illustrates the characteristic XPS N1s spectrum of paper containing polydiallyldimethylammonium chloride (PDADMAC), and the third example is of a handsheet containing 0.2% PDADMAC and 0.5% anionic polyacrylamide (A-PAM) on dry pulp. The effect of paper strength additives on the fiber surface or between fibers on paper strength is explained.

## Materials and methods

### Handsheets: preparation and strength properties

The various polymer additives were added to an LBKP slurry (Table 1). The standard handsheets with a grammage of 60 g/m$^2$ were made at pH 7.5. PDADMAC was used as a retention aid for A-PAM. The wet handsheets were pressed at 345 kPa for 5 min and dried at 105°C for 10 min in a convection oven. The tensile strength of the paper sheet was determined according to JIS P8113.

### Preparation of samples for XPS characterization

The handsheets were cut into pieces approximately 5 × 10 mm, which were mounted in the analysis chamber of the XPS instrument. Films of polymer (see Tables 4, 5, below)

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**Table 1.** Effects of PDADMAC and A-PAM on dry tensile strength

| No. | Paper strength agents | Addition level (% on pulp) | Dry tensile strength (N·m/g) | pH of paper stock |
|---|---|---|---|---|
| 1 | Blank | 0.00 | 44.7 (1.00) | 7.3 |
| 2 | PDADMAC | 0.20 | 50.5 (1.13) | 7.5 |
| 3 | PDADMAC | 0.20 | 56.4 (1.26) | 7.5 |
| | A-PAM | 0.50 | | |

Pulp: LBKP (hardwood-bleached kraft pulp).
PDADMAC, polydiallyl dimethlammonium chloride; A-PAM, anionic polyacrylamide.

were prepared by applying the aqueous polymer solution (5%) to a stainless steel plate (5 × 10mm) and heating at 105°C for 10min. The films were cooled to 22° ± 2°C in a desiccator. The PDADMAC and A-PAM powders, which were prepared by pouring 40% PDADMAC and 15% A-PAM aqueous solutions into acetone, respectively, were fixed to an electrically conductive adhesive-coated tape (5 × 10mm).

### Equipment

All analyses were performed on an AXIS-HSi spectrometer from Shimadzu/Kratos. Monochromatic AlK$\alpha$ radiation was used to excite the electrons. Unmonochromated AlK$\alpha$ radiation was also used for comparison. For all analyses, a low-energy electron flood gun was applied to neutralize the specimen surfaces. The background pressure during the analysis was in the low 0.1$\mu$Pa range. Curve fitting and quantification were performed using version 1.4.0 provided on the system. Binding energies of all spectra were related to carbon 1s(C-C) at 285eV.

## Results and discussion

### Analysis conditions

#### *Effects of charging compensation*

For a successful XPS analysis of paper, the surface of which was insulating, minimization of sample charging was the critical factor. An unmonochromated X-ray source (AlK$\alpha$) generates low-energy electrons as the bremsstrahlung component of the radiation passes through the aluminium foil separating the anode from the sample chamber. For this reason, unmonochromated XPS of an insulator does not normally require any additional charge compensation, as shown in Fig. 1a. However, a monochromated source does not generate such low-energy electrons, so not only is the intensity of the spectrum low but the chemical shifts are large, as shown in Fig. 1b. Sample charging can shift the photoelectron peak tens (15eV in Fig. 1a,c) or hundreds (221eV in Fig. 1b,d) of electron volts. Furthermore, the intensity of the spectrum of monochromated AlK$\alpha$ is six times that of unmonochromated AlK$\alpha$ in charging compensation, as shown in Fig. 1d,c.

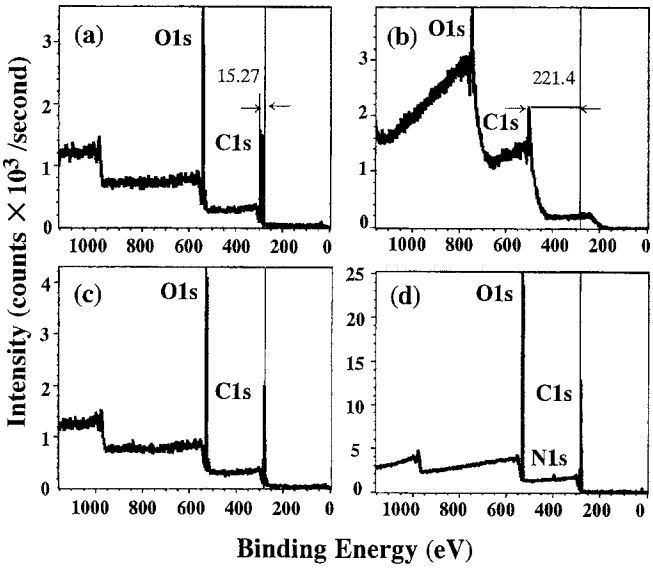



**Fig. 1.** X-ray Photoelectron spectroscopic (XPS) survey spectra of an anionic polyacrylamide (A-PAM)-containing handsheet. **a,c** Unmonochromated AlK$\alpha$ source. **b,d** Monochromated AlK$\alpha$ source. **a,b** Electron flood gun off. **c,d** Electron flood gun on. Measuring conditions: voltage 15kV, current 10mA, pass energy 80eV, sweep times 5

#### *Resolution*

For the more precise identification of chemical states, excellent energy resolution is an important factor. The C core-level spectra for a handsheet sample in this study were compared at different pass energies (PEs), as shown in Fig. 2a. The peaks of the $C_1$, $C_2$, $C_3$, and $C_4$ components derived by curve fitting are shown in Fig. 2b. The full width at half-maximum (FWHM) values of the $C_1$, $C_2$, $C_3$, and $C_4$ components derived at different PEs are given in Table 2. Excellent energy resolution was obtained at a pass energy of 5eV (Table 2) but with a considerable sacrifice of intensity, which, for example, reduces from the 41 × $10^3$ counts of PE 80eV to 1 × $10^3$ counts of PE 5eV (Fig. 2a). A good compromise between intensity and energy resolution is obtained at 10eV pass energy if the integrating times are lengthened 10–50 times. Figure 3a shows C1s spectra recorded for the same sample as that in Fig. 2 under the conditions shown in Table 3. The FWHM of the $C_1$, $C_2$, $C_3$, and $C_4$ components are 1.13, 1.07, 1.08, and 1.09eV, respectively; and the intensity is almost the same as that of PE 40eV (Fig. 2a). With the same instrument settings, but using the unmonochromated AlK$\alpha$ source, the widths are 1.51, 1.30, 1.40, and 1.40eV, respectively, as shown in Fig. 3b. The details of the XPS analyses are listed in Table 3.

### XPS of PDADMAC and A-PAM

Table 4 (sample 1) shows the C1s and N1s core-level spectra data derived by curve fitting for the PDADMAC powder.

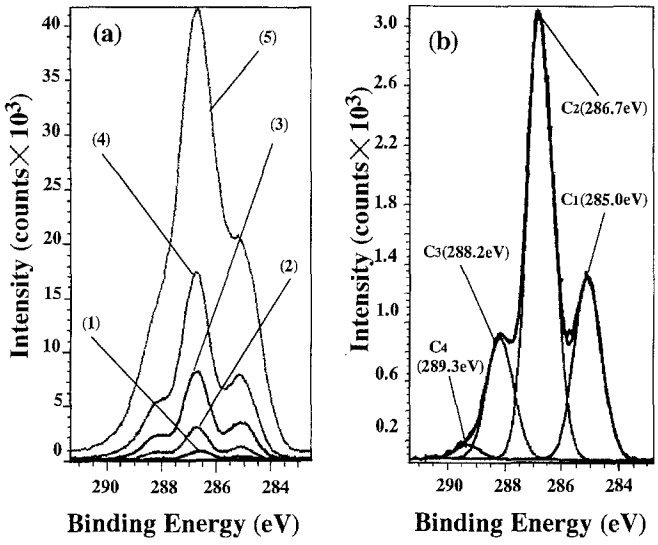



**Fig. 2.** **a** Comparison of the C1s core-level spectra for a hardwood bleached kraft pulp (LBKP) handsheet sample in this study at different pass energies (PEs). (*1*) PE 5eV; (*2*) PE 10eV; (*3*) PE 20eV; (*4*) PE 40eV; (*5*) PE 80eV. **b** High-resolution C1s XPS at PE 10eV. X-ray source was monochromated AlK$\alpha$; voltage 15kV; current 10mA; sweep times 10; electron flood gun on

**Table 2.** FWHM of core-level components

| Pass energy (eV) | FWHM of components (eV) | | | |
|---|---|---|---|---|
| | $C_1$ | $C_2$ | $C_3$ | $C_4$ |
| 5 | 1.08 | 1.04 | 1.06 | 1.05 |
| 10 | 1.12 | 1.06 | 1.10 | 1.09 |
| 20 | 1.15 | 1.09 | 1.15 | 1.15 |
| 40 | 1.19 | 1.19 | 1.24 | 1.19 |
| 80 | 1.49 | 1.40 | 1.49 | 1.35 |

See Fig. 2.
FWHM, full width at half-maximum.

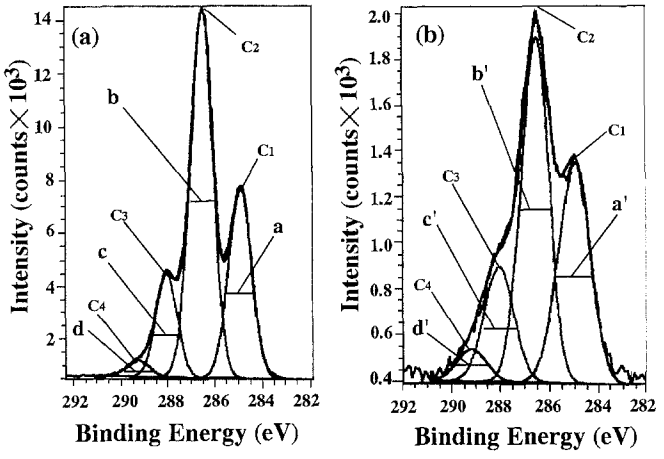



**Fig. 3.** C1s core-level spectrum for the same sample as that of Fig. 2. The measuring conditions are shown in Table 3. **a** Monochromated AlK$\alpha$. **b** Unmonochromated AlK$\alpha$. $C_1$, $C_2$, $C_3$, $C_4$: see Fig. 2b. Full width at half-maximum (FWHM): *a*, 1.13eV; *b*, 1.07eV; *c*, 1.08eV; *d*, 1.09eV; *a'*, 1.51eV; *b'*, 1.30eV; *c'*, 1.40eV; *d'*, 1.40eV

**Table 3.** Conditions for XPS analysis

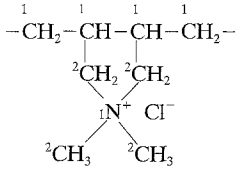
| | |
|---|---|
| XPS | AXIS-HSi |
| X-ray source | Monochromatized AlK$\alpha$ |
| Output | 15kV × 10mA |
| Vacuum level | $<5 \times 10^{-7}$Pa |
| Data processing | Version 1.4.0 (Kratos) |
| Analyzer pass energy (eV) | 10 |
| Integration times | 50 |
| Analyzer mode | HYBRID mode |
| Sample size (mm × mm) | 5 × 10 |

XPS, X-ray photoelectron spectroscopy.

**Table 4.** XPS analysis of PDADMAC with and without heating

| Parameter | C1s | | | N1s | |
|---|---|---|---|---|---|
| | 1 | 2 | 3 | 1 | 2 |
| Sample 1 | | | | | |
| BE (eV) | 285.0 | 286.3 | | 402.6 | |
| FWHM (eV) | 1.19 | 1.32 | no | 1.15 | no |
| Area (%) | 49.9 | 50.1 | | 100 | |
| Sample 2 | | | | | |
| BE (eV) | 285.0 | 286.2 | 288.1 | 402.6 | 399.7 |
| FWHM (eV) | 1.19 | 1.32 | 2.04 | 1.15 | 1.16 |
| Area (%) | 50.0 | 43.6 | 6.4 | 66.5 | 33.5 |

Structure of PDADMAC



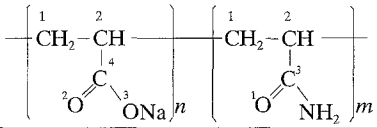

Sample 1, PDADMAC powder sample precipitated from 40% PDADMAC aqueous solution by pouring into acetone; sample 2, film sample formed by heating PDADMAC aqueous solution at 105°C for 10min.

The C1s spectra data corresponded to the $=CH-CH_2-$ structure and the $-(CH_2)_2-N^+-(CH_3)_2$ structure at binding energies (BEs) of 285.0 and 286.2eV, respectively. The difference in both areas is 0.2%, as shown in Table 4, which indicates that the error in XPS measurements is low. The N1s XPS data show the component at BE 402.6eV, attributable to the $-(CH_2)_2-N^+-(CH_3)_2$ structure.

When aqueous PDADMAC was heated to dryness at 105°C for 10min, the expected heat denaturation was confirmed by the appearance of a new C1s component at about BE 288.1eV and an N1s component at about BE 399.7eV, as shown in Table 4 (sample 2).

In Table 5, the C1s core-level spectra data for A-PAM obtained with and without heating at 105°C for 10min show carbon of the $-CH_2-CH-CONH_2$ and $-COOH$ bonds of A-PAM at BE 285.0, 285.4, 288.5, and 289.3eV, respectively. The BE of A-PAM nitrogen at 399.9eV is indicated. The three O1s components of A-PAM are 531.6, 532.2, and 533.3eV, as shown in Table 5. The actual C1s area (27.3%) of $-CONH_2$ + $-COONa$ is lower than that in theory (33.3%). The origins are not understood at present. The data of Table 5 are in good agreement with the literature values (27.0%).[26]

**Table 5.** XPS analysis of A-PAM with and without heating

| Parameter | C1s | | | | N1s | O1s | | |
|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | | 1 | 2 | 3 |
| Sample 1 | | | | | | | | |
| BE (eV) | 285.0 | 285.4 | 288.5 | 289.3 | 399.9 | 531.6 | 532.2 | 533.3 |
| FWHM (eV) | 1.04 | 1.10 | 1.15 | 1.22 | 1.31 | 1.30 | 1.43 | 1.46 |
| Area (%) | 36.3 | 36.4 | 24.4 | 2.9 | 100 | 80.2 | 9.9 | 9.9 |
| Sample 2 | | | | | | | | |
| BE (eV) | 285.0 | 285.4 | 288.5 | 289.3 | 399.9 | 531.6 | 532.2 | 533.3 |
| FWHM (eV) | 1.04 | 1.10 | 1.15 | 1.22 | 1.31 | 1.30 | 1.43 | 1.46 |
| Area (%) | 36.5 | 36.3 | 24.3 | 3.0 | 100 | 80.0 | 10.0 | 10.0 |
| Sample 3 | | | | | | | | |
| BE (eV) | 285.0 | 285.4 | 288.5 | | 399.8 | 531.5 | | |
| FWHM (eV) | 1.01 | 1.10 | 1.15 | no | 1.31 | 1.34 | no | no |
| Area (%) | 36.0 | 36.0 | 27.0 | | 100 | 100 | | |
| Structure of A-PAM ($n$ = 10%, $m$ = 90%): |  | | | | | | | |

Sample 1, A-PAM powder sample precipitated from pouring 15% A-PAM aqueous solution into acetone; sample 2, film sample formed by heating A-PAM aqueous solution at 105°C for 10 min; sample 3, literature values[26] of polyacrylamide (PAM).

## XPS of handsheets with and without paper strength additives

### *Carbon signal*

The carbon atoms in woody materials were divided into four categories based on their chemical shifts.[15] Figure 4b shows a high-resolution C1s signal for paper without additives. The total signal can be resolved into four peaks ($C_1$–$C_4$) due to carbons at different oxidation levels: $C_1$ refers to unoxidized carbon, $C_2$ refers to carbon with one bond to oxygen (i.e., O–C), $C_3$ refers to carbon with two bonds to oxygen (i.e., O–C–O and C=O), and $C_4$ refers to carbon with three bonds to oxygen (i.e., O–C=O). $C_2$ and $C_3$ components arise mainly from cellulose and $C_1$ and $C_4$ mainly from lignin and wood extractives.[14,15,24,25]

Figure 5b shows the C1s spectra of XPS for PDADMAC-containing paper. The C1s peak shows five components. The new $C_5$ fraction of 286.2 eV arises from the $-(CH_2)_2-N^+-(CH_3)_2$ structure of PDADMAC (Table 4).

In the case of the (PDADMAC + A-PAM)-containing sheet (Fig. 6b), the C1s peak has been curve-fitted with seven components. The new $C_6$ and $C_7$ fractions at 285.4 and 288.5 eV are attributable to $=CH-CH_2-$ and $-CONH_2$, respectively.

Although the C1s peaks ($C_5$, $C_6$, $C_7$) for PDADMAC and A-PAM are detected apparently on the surface of the paper to which PDADMAC and PDADMAC + A-PAM were added, these peak areas ($C_5 + C_6 + C_7$) are much smaller than total peak areas ($C_1$–$C_7$) of C1s in the sheet. For example, the mass concentration of $C_5 + C_6 + C_7$ components to total mass of C atoms is only 2.55%. The C1s spectra is therefore not suitable for identifying the chemical covalence on the paper surface arising from small amounts of strength additive.

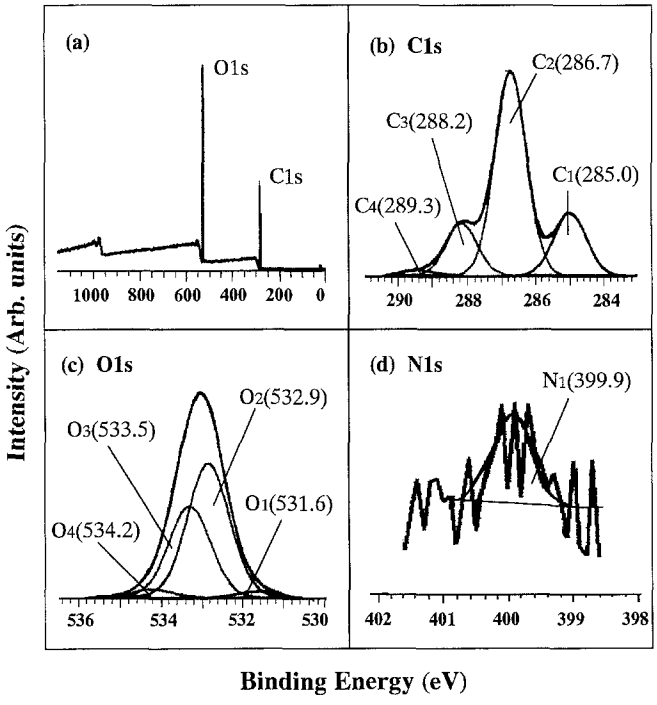



**Fig. 4.** XPS spectra for the LBKP sheet without additives. **a** Survey spectra. **b** C1s peak. **c** O1s peak. **d** N1s peak

### *Oxygen signal*

Studies of the O1s peak of wood-derived materials are rare in the literature, because of its complex shift behavior compared with that of the C1s peak. Koubaa et al.[25] classified the oxgen atoms in woody materials into three categories based on the literature of Ahmed et al.,[16] Kamden et al.,[20] and Hua et al.[22]

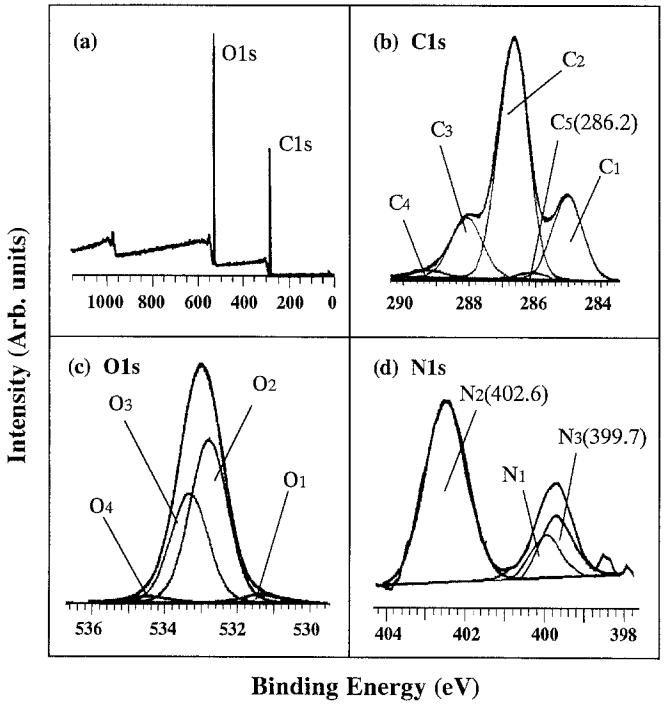



**Fig. 5.** XPS spectra for the LBKP sheet containing polydiallyl dimethylammonium chloride (PDADMAC) at the 0.2% level on dry pulp. **a** Survey spectra. **b** C1s peak. **c** O1s peak. **d** N1s peak

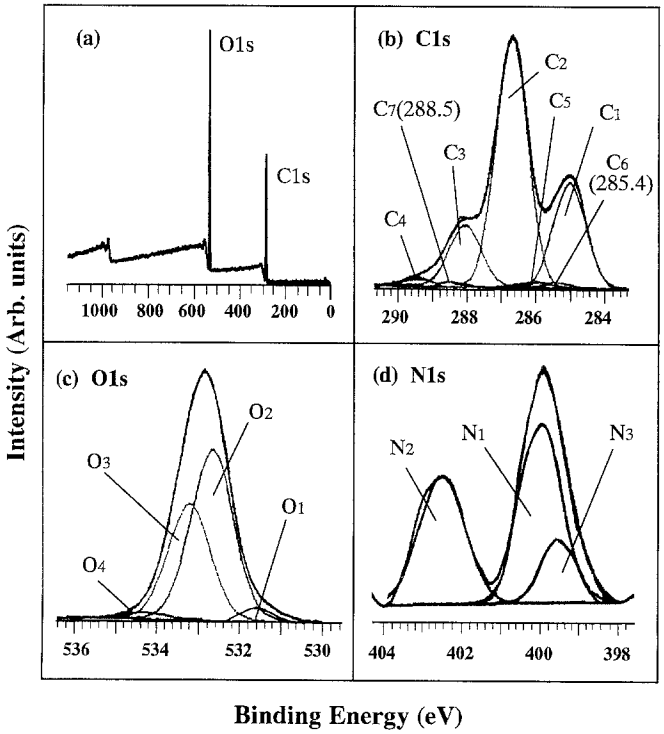



**Fig. 6.** XPS spectra for the LBKP sheet added with PDADMAC at the 0.2% level and with A-PAM at the 0.5% level on dry pulp. **a** Survey spectra. **b** C1s peak. **c** O1s peak. **d** N1s peak

In our study curve-fitting on the O1s spectra was performed according to *High Resolution XPS of Organic Polymers*,[26] a highly authoritative book on XPS data. The O1s spectra analysis of the additive-free sheet give $O_1$, $O_2$, $O_3$, and $O_4$ components at BE 531.6, 532.9, 533.5, and 534.2 eV, respectively, as shown in Fig. 4c. The BEs of $O_2$ and $O_3$ are in an excellent agreement with those of cellulose reported in the literature.[26] $O_1$ and $O_4$ components arise mainly from lignin and wood extractives.

The O1s peaks of the PDADMAC-containing sheet (Fig. 5c) and of the (PDADMAC + A-PAM)-containing sheet (Fig. 6c) are similar to those of additive-free paper.

In the PDADMAC + A-PAM added case (Fig. 6c), the peak area of the $O_1$ fraction at 531.6 eV increased slightly, arising from a $-CONH_2$ structure. However, for the same reason as for the C1s, because the mass concentration of O of $-CONH_2$ is only 1.2% of the total mass of O atoms, it is difficult to identify the chemical covalence caused by small amounts of strength additive from the O1s spectra of the paper.

*Nitrogen peaks*

The survey spectra of an LBKP sheet is shown in Fig. 4a. The carbon and oxygen can be easily detected, but a nitrogen peak is difficult to find. Although the nitrogen originally present in the sheet was found by increasing the integrating time, the amounts were small, less than 0.08% of the total mass of the C, O, and N atoms (Table 6). It is therefore possible to identify the chemical covalences arising from small amounts of additive containing nitrogen on the paper by analyzing the N1s spectra.

The N1s core-level spectrum for an additive-free sheet (Fig. 4d) has been curve-fitted with components arising from the nitrogen of the $-CO-NH-$ structure at BE 399.9 eV,[26] which originates from protein in pulps.

Figure 5d shows the high-resolution and curve-fitted XPS of N1s signals for PDADMAC-containing paper. It reveals two new peaks not present in the signals for additive-free paper: the N fractions of the $-(CH_2)_2-N^+-(CH_3)_2$ structure at BE 402.6 eV and of heat denaturation at BE 399.7 eV.

The N1s spectra for paper containing PDADMAC + A-PAM (Fig. 6d) shows these $N_1$–$N_3$ three components to be the same BEs as for the PDADMAC-containing sheet. However, a considerable increase in the area of the $N_1$ fraction at 399.9 eV, from 3 to 14 eV·counts (Table 6), was observed in this case. Because $N_1$ is associated with the $-CONH_2$ structure, this increase indicates the presence of A-PAM on the paper surface.

Furthermore, the mass concentration of N associated with PDADMAC on the PDADMAC-containing sheet surface was 0.33% ($N_2$ + $N_3$), and that of N associated with A-PAM on the (PDADMAC + A-PAM)-containing sheet surface was 0.19% (0.27–0.08) as shown in Table 6. These figures are much larger than the additive levels (N of

**Table 6.** XPS N1s peaks analysis of additive-free sheet, PDADMAC-containing sheet, and (PDADMAC + A-PAM)-containing sheet

| BE of fraction (eV) | No additives | | PDADMAC | | PDADMAC + A-PAM | |
|---|---|---|---|---|---|---|
| | Area[a] | Mass %[b] | Area[a] | Mass %[b] | Area[a] | Mass %[b] |
| $N_1$ (399.9) | 4 | 0.08 | 3 | 0.05 | 14 | 0.27 |
| $N_2$ (402.6) | – | – | 13 | 0.24 | 9 | 0.18 |
| $N_3$ (399.6) | – | – | 5 | 0.09 | 7 | 0.14 |

[a] This is raw area of N1s peak, the unit is eV·counts. The counts are those of net peak intensity.
[b] Mass concentration of nitrogen fraction is the percentage mass of the nitrogen fraction to total mass of C, O, and N atoms in the sample.

PDADMAC is 0.017% on pulp; N of A-PAM is 0.09% on pulp), indicating that the polymer additives used in this study are mainly distributed on the fiber surface.

Effects of strength additives on the dry tensile strength

Dry tensile strengths of handsheets containing PDADMAC + A-PAM at pH 7.5 and of handsheets with no additive and with only PDADMAC are shown in Table 1. The dry tensile strength of handsheets containing only PDADMAC is somewhat higher (13%) than that of the additive-free paper. It is guessed that a larger fiber and fiber contact area is created through networks formed by PDADMAC adsorbed on the surface of fibers and between fibers when sheets were formed.

With the addition of A-PAM, a significant increase (26%) in dry tensile strength was obtained. It was attributed to hydrogen bonds formed between A-PAM/A-PAM and A-PAM/cellulose through the presence of A-PAM on the fiber surface.

## Conclusions

The conditions for XPS measurements of handsheets containing small amounts of paper strength additives were discussed. Based on the evidence, the use of flood guns and monochromated X-rays are recommended. The XPS chemical shift data obtained for A-PAM and PDADMAC are in good agreement with values reported in the literature.

The observed N1s chemical shifts for handsheets containing PDADMAC and PDADMAC + A-PAM were compared with those of PDADMAC alone and A-PAM alone. XPS analysis made it possible to determine chemical covalences on a paper surface arising from small amounts of polymer additive. The nitrogen concentration detected on the handsheet surfaces by XPS analysis indicate that polymer additives used in this study are distributed mainly on the fiber surface.

An increase in dry tensile strength for paper sheet containing PDADMAC + A-PAM was attributed to hydrogen bonds formed between A-PAM/A-PAM and A-PAM/cellulose, and the networks formed by PDADMAC and A-PAM on the fiber surface.

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