

# Function Mechanisms of Polyamines in Rosin Sizing under Neutral Papermaking Conditions

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**ABSTRACT:** The surface analyses of the papers sized with a rosin emulsion (RE) and five typical polyamines, polyallylamine (PAAm), polyvinylamine (PVAm), polyethyleneimine (PEI), poly(diallyldimethylammonium chloride) (PDADMAC), and poly(dimethylamino ethyl methacrylate) (PDMAEMA), were performed using a X-ray photoelectron spectrometer. The results show that the chemical states of the polyamines on the outermost surfaces of the papers changed significantly during the neutral rosin sizing. The five polyamines could react with carboxyl groups of the fibers to form urethane linkages at  $400.0 \pm 0.1$  eV, which resulted in absorption of the polyamines onto the fibers. Only PAAm and PVAm could combine with RE to form urethane linkages at  $400.7-0.1$  eV, which were related deeply to sizing effectiveness. The polyamines distributed mainly on the surfaces of the fibers. The concentrations of PAAm and PVAm on the surfaces of the sized papers were much larger than those of PEI, PDMAEMA, and PDADMAC. A larger sizing degree was related to a larger C1 component at 285.0 eV (C—C) in the C1s XPS spectra of the sized papers. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2185–2190, 2001

**Key words:** paper sizing; rosin; polyamines; function mechanisms; XPS

## INTRODUCTION

In papermaking, internal sizing is the process of providing paper and paperboard with resistance to liquid wetting, penetration, and absorption by the use of sizing agents during the paper forming. Rosin with alum has been a dominant sizing agent since 1807. In the recent years, however, papermaking conditions have been rapidly shifting from acidic to neutral-alkaline regions for some technological and economic reasons. Under these conditions, conventional rosin sizing has

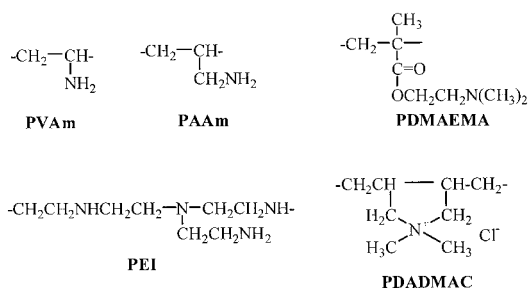
become difficult, partly because alum has a low cationicity at elevated pHs and loses its ability to orient rosin size onto pulp surfaces.<sup>1–3</sup> Polyamines have been tested to improve the cationicity of alum at higher pHs so that the conventional rosin sizing can be applied to neutral papermaking systems.

In the previous articles<sup>4,5</sup> we reported that the four commercial rosin emulsions with the polyamines exhibited effective sizing in the pH region from 4 to 8. The molecular structures of the polyamines greatly influenced their efficiency in the rosin sizing. Polyallylamine (PAAm) and polyvinylamine (PVAm) with linear structures were more effective than polyethyleneimine (PEI) with branched structures. The main objective of this

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**Figure 1** The molecular structures of the polyamines used in this study.

study is to characterize the changes in the surface chemistry of the papers sized with a rosin emulsion (RE) and five typical polyamines using X-ray photoelectron spectroscopy (XPS). It is expected that the results of this study will help us to better understand the role of the polyamines in the neutral rosin sizing and the mechanism of bond formation on the surfaces of the papers.

## EXPERIMENTAL

### Materials

A commercial bleached hardwood kraft pulp was used. The pulp was beaten to a Canadian Standard Freeness (CSF) of 410 mL in a TAPPI standard beater. A rosin emulsion size (RE) was obtained from a size manufacturer. Poly(dimethylamino ethyl methacrylate) (PDMAEMA)<sup>6</sup> and PVAm<sup>7</sup> were prepared based on the method of Tanaka and Senju. The average molecular weights of the two polyamines were 36,000 and 45,000, respectively, according to size exclusion chromatography using poly(ethylene oxide)s (Tosoh Co., Japan) as standard polymers. Poly(diallyldimethylammonium chloride) (PDADMAC) and PAAm were obtained from the Aldrich Co., and had average molecular weights of 53,000 and 57,000, respectively. The molecular structures of the polyamines used in this study are shown in Figure 1.

### Sizing Procedures

Handsheets with a basis weight of about 60 g/m<sup>2</sup> were formed according to TAPPI Test Method T2050m-88. The sizing effectiveness was evaluated according to Japan Industrial Standard P8122: A drop of 1% ferric chloride solution is applied to the upper surface of a sample folded for flotation. Immediately, the sample is floated on a

2% solution of ammonium thiocyanate. A sizing degree is evaluated by the time from the beginning of flotation to the development of a bright red color.

### XPS Measurement

All XPS analyses were performed on a Shimadzu-Kratos AXIS-HSi X-ray photoelectron spectrometer. Monochromatic aluminum X-rays ( $K\alpha = 1486.7$  eV) at 150 W were used. A low-energy electron flood gun provided specimen neutralization. Samples were tilted at 90 degrees with respect to the analyzer. Curve fitting and quantification were performed using routines provided in the software on the spectrometer. All binding energies of the spectra were related to C1 (C—C) at 285.0 eV.

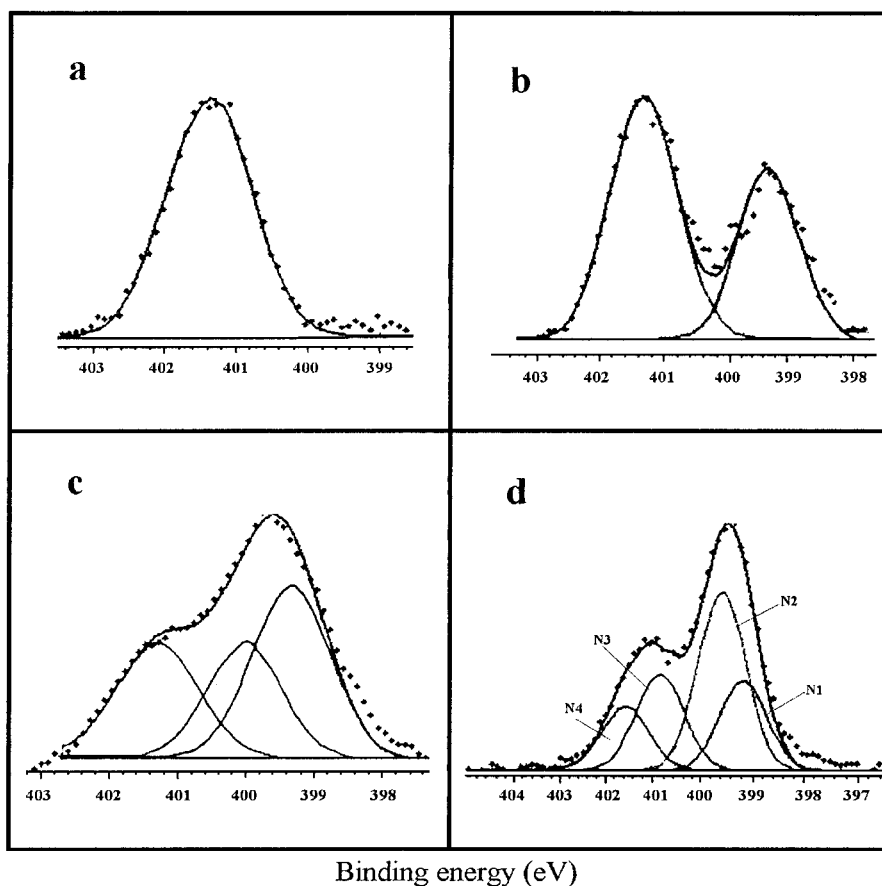
## RESULTS AND DISCUSSION

### Changes in Chemical States of the Polyamines

Figure 2 shows the high resolution N1s XPS spectra of PAAm. It can be seen from the spectra that the chemical states of PAAm in the LBKP sheets are quite different from that of PAAm powder. There is only one signal at 401.4 eV in the spectrum of PAAm powder [Fig. 2(a)]. It originates from the ammonium groups ( $-\text{NH}_3^+-$ ) of PAAm.<sup>8,9</sup> When aqueous PAAm was heated to dryness at 105°C for 10 min, a new peak at 399.3 eV occurred in Figure 2(b). Based on the standard spectra,<sup>10,12</sup> the signal is assigned to amino groups. The relative areas of the two peaks are 60 and 40%, respectively, indicating that about 40% of the ammonium groups of PAAm were converted to amino groups after heating.

The spectrum [Fig. 2(c)] of the LBKP sheet added with only PAAm consists of three peaks, N1 (399.3 eV), N2 (400.0 eV,  $-\text{COO}-\text{NH}-$ ), and N4 (401.4 eV). The relative areas of the three peaks are 43, 27, and 30%, respectively. These data demonstrate that the nitrogen atoms of PAAm in the sheets are present in the three chemical states. About 30% of the nitrogen atoms reacted with carboxyl groups of the fibers to form urethane linkages.

A new peak N3 at 400.7 eV appeared in the XPS spectrum [Fig. 2(d)] of the LBKP sheets sized with a rosin emulsion (RE) and PAAm. The peak may originate from urethane linkages formed between PAAm and RE. Like PAAm, PVAm was also effective in the neutral rosin sizing. The



**Figure 2** Changes in the binding energies of PAAm before and after rosin sizing: a. PAAm powder; b. PAAm heated at 105°C for 10 min; c. LBKP sheet added with 2% of PAAm; d. LBKP sheet sized with 0.5% of RE and 2% of PAAm.

changes in the chemical states of PVAm were quite similar to those of PAAm.

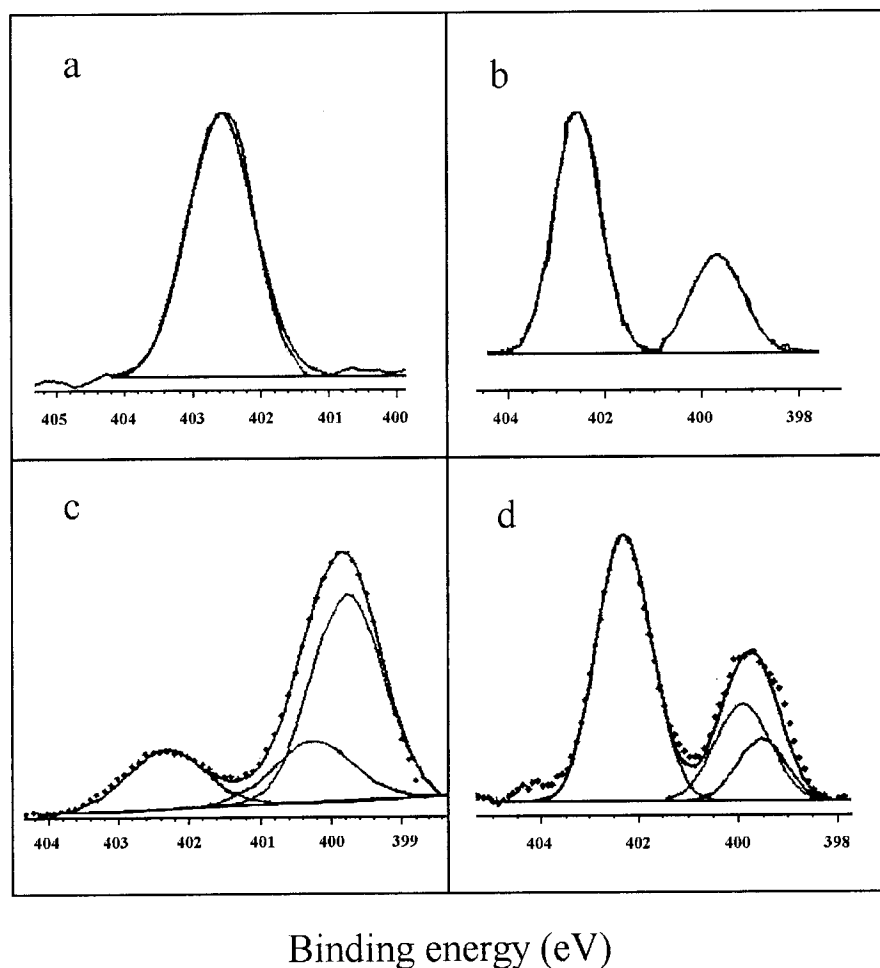
The previous articles<sup>4,5</sup> described that PDADMAC and PEI were ineffective in the neutral rosin sizing. The N1s XPS spectra of PDADMAC in Figure 3 illustrate that the changes in the chemical states of PDADMAC were different from those of PAAm during the sizing. When aqueous PDADMAC was heated to dryness at 105°C for 10 min, two peaks occurred, as shown in Figure 3(b). The peak at 402.6 eV originates from quaternary ammonium groups, and the peak at 399.7 may be assigned to the amino groups degraded from the ammonium groups of PDADMAC.<sup>9</sup> The relative amounts of the two peaks indicate that the heating made about 30% of the ammonium groups degrade to the amino groups.

The comparison of Figure 2(d) and Figure 3(d) shows that the peak at 400.7 eV was not formed in the LBKP sheets sized with RE and PDADMAC. The results suggest that though PDADMAC can combine with carboxyl groups of the

pulp [Fig. 3(c)], it hardly reacted with rosin to form urethane linkages during the sizing. This may be a reason for poor performance of PDADMAC in the neutral rosin sizing. PEI and PDMAEMA exhibited similar changes in the chemical states as did PDADMAC before and after the rosin sizing.

#### Nitrogen Signals and Sizing Effectiveness

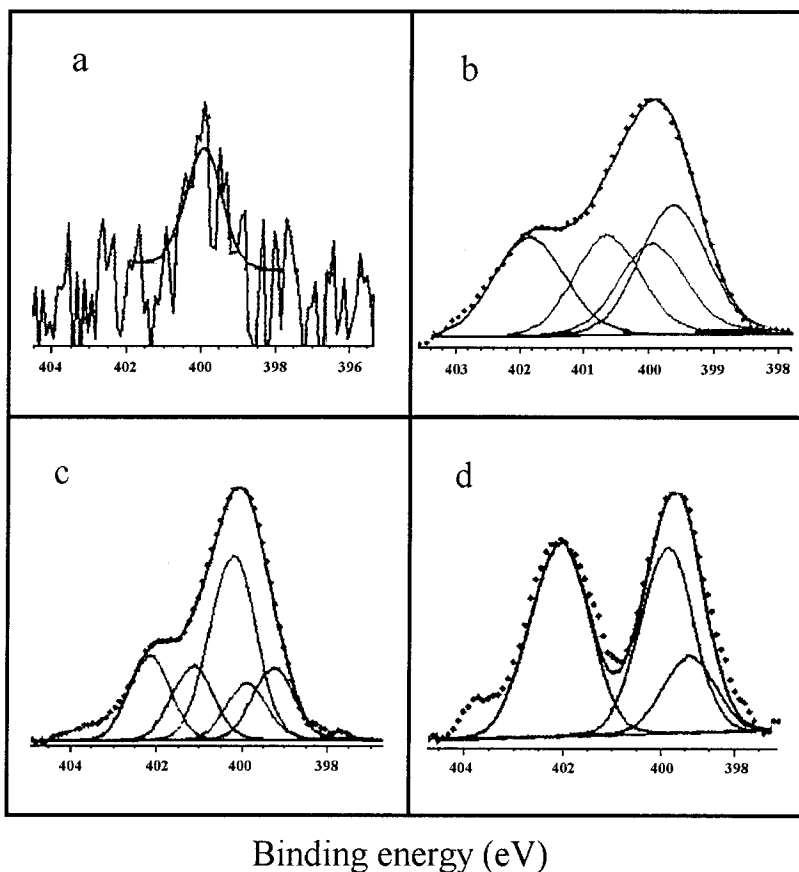
Figure 4 shows high-resolution N1s XPS spectra of the LBKP sheets sized with RE + PVAm [Fig. 4(b)], RE + PEI [Fig. 4(c)], and RE + PDMAEMA [Fig. 4(d)]. Based on the comparison of these spectra with Figures 2(d) and 3(d), it can be found that the peak at  $400.0 \pm 0.1$  eV is present in all of the five spectra. As described above, this signal originate from the  $-\text{COO}-\text{NH}-$  structures. Thus, the facts prove that the urethane linkages formed between the amino groups of the polyamines and carboxyl groups of the fibers, and resulted in absorption of the polyamines onto the pulp.



**Figure 3** Changes in the chemical states of PDADMAC before and after rosin sizing: a. PDADMAC powder; b. PDADMAC heated at 105°C for 10 min; c. LBKP sheet added with 2% of PDADMAC; d. LBKP sheet sized with 0.5% of RE and 2% of PDADMAC.

The peak N3 at 400.7  $\pm$  0.1 eV occurs in the spectra of the sheets sized with RE + PAAm [Fig. 2(d)] and RE + PVAm [Fig. 4(b)], and the relative amount of N3 is 22% in the spectrum of RE + PAAm and 23% in the spectrum of RE + PVAm. On the basis of the standard spectra,<sup>8,9</sup> N3 may be assigned to urethane linkages formed between RE and the polyamines. On the other hand, the sizing degrees of the sheets sized with RE + PAAm and RE + PVAm were 31 and 32 s, respectively. However, there is no N3 peak in the spectra of the sheets sized with RE + PDMAEMA [Fig. 3(d)], RE + PEI [Fig. 4(c)], and RE + PDMAEMA [Fig. 4(d)], and the sheets exhibited low sizing degrees, 0, 3, and 6 s, respectively. These results, therefore, reveal that the formation of the urethane linkages at 400.7 eV between RE and the polyamines is a key step for effective rosin sizing.

As shown in Table I, the much larger concentrations of PAAm and PVAm on the surfaces of the sized papers is another explanation for their large effectiveness in the neutral rosin sizing. The nitrogen contents (Ns) on the outermost surfaces of the sheets sized with RE + PAAm and RE + PVAm were about 10 times larger than the Kjeldahl nitrogen contents (Nk) in the sheets. The Ns contents of the sheets sized with RE + PDMAEMA, RE + PEI, and RE + PDMAEMA were about five to six times larger than their Nk contents. The larger concentrations of PAAm and PVAm on the outermost surfaces of the sheets must increase the chances to react with RE so that more rosin can be retained on the surfaces of the fibers. This is consistent with the results of the chemical analysis that PVAm and PAAm



**Figure 4** High resolution N1s X-ray photoelectron spectra of the papers sized with RE and the polyamines: a. Blank sheet; b. RE + PVAm; c. RE + PEI; d. RE + PDMAEMA.

could retain more rosin on the pulp than the other three polyamines did.<sup>5</sup>

#### Carbon Signals and Sizing Effectiveness

Figure 5 shows the high resolution C1s XPS spectra of the sheets sized with RE and the five poly-

**Table I** The Nitrogen Contents of the Polyamines Determined by XPS and Kjeldahl Method

Polyamine	Nk (%)	Ns (%)	N3 (%)
PAAm	0.11	1.59	22
PVAm	0.18	1.66	23
PEI	0.32	1.58	trace
PDMAEMA	0.13	0.76	trace
PDADMAC	0.14	0.86	—

Nk: Kjeldahl nitrogen contents in the sized papers.

Ns: Nitrogen contents on the surfaces of the sized papers (per 100 g atoms).

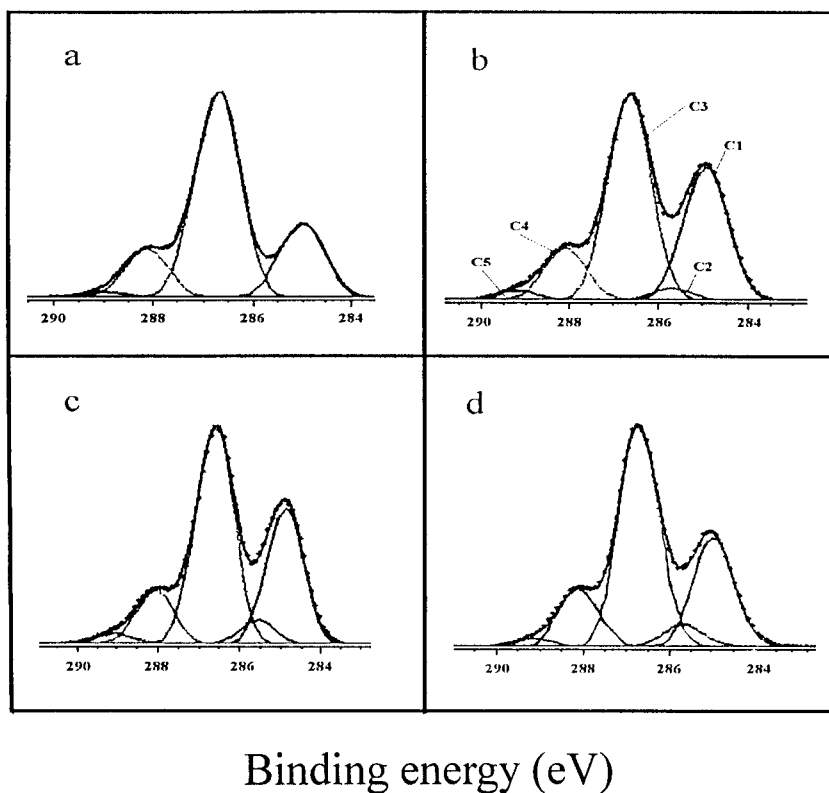
N3: The relative areas of the peaks at  $400 \pm 0.1$  eV in N1s XPS spectra of the sized papers.

Trace <1%.

amines. The chemical shifts relative to C1 (C—C) at 285.0 eV were  $0.7 \pm 0.2$  eV for C2 (C—N),  $1.7 \pm 0.1$  eV for C3 (C—O),  $3.1 \pm 0.4$  for (O—C—O or C=O), and  $4.4 \pm 0.3$  for C5 (O=C—O). The assignments are in good agreement with the previous classification of carbon atoms in woody materials.<sup>10–13</sup>

Many studies<sup>14–16</sup> have shown that rosin size must be retained on the fibers as much as possible to achieve effective sizing. The results in Table II show that a polyamine with a smaller molecular geometric size can retain more rosin size on fibers so that a better sizing effectiveness can be achieved. But the rosin amounts in Table II were determined by the method of solvent extraction, and were an indicator for rosin size in the sheets. To examine the distribution of RE on the sheet surfaces, the C1 components in C1s XPS spectra of the sheets were investigated.

The C1s XPS spectrum of rosin (abietic acid) consist of C1 (92%), C3 (4%), and C4 (4%). Therefore, the relative amounts of C1 compo-



**Figure 5** High resolution C1s XPS spectra of the papers sized with RE and the polyamines: a. Blank sheet; b. RE + PVAm; c. RE + PAAm; d. RE + PEI.

ment can be an indicator for rosin size on sheet surfaces. It can be seen from Figure 5 and Table II that the C1 components in the spectra of the sheets sized with RE + PEI, RE + PAAm, and RE + PVAm were 26, 32, and 33%, and the sizing degrees of the sheets were 3, 31, and 32 s, respectively. A larger C1 component is related to a larger sizing degree.

**Table II** The Sizing Degrees and C1 Components in C1s XPS Spectra of the Sized Papers<sup>a</sup>

Polyamine	Sizing Degree (s)	C1 at 285.0 eV (%)	RE Retention (%)
Blank	—	23	—
PVAm	32	33	84
PAAm	31	32	79
PEI	3	26	64

<sup>a</sup> The amounts of RE and the polyamines added to slurry were 0.5 and 2% on pulp, respectively.

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