

FUNCTIONS OF POLYAMINES IN ROSIN SIZING UNDER NEUTRAL PAPERMAKING CONDITIONS*

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Abstract Functions of the polyamines in neutral rosin sizing were investigated using X-ray photoelectron spectroscopy (XPS) and laser diffraction particle analysis. The polyamine with a higher charge density and a smaller unite size could retain more rosin and cover larger fiber surfaces. The XPS spectra demonstrated that polyallylamine (PAAm) and polyvinylamine (PVAm) could react with a rosin size to form a $-\text{OC}-\text{N}-\text{CO}-$ structure, but polydimethylamino ethyl methacrylate (PDMAEMA) could not. The formation of this structure may be a key step for effective sizing.

Keywords Papermaking, Polyamine, Neutral rosin sizing, XPS spectroscopy, Laser diffraction particle analysis

INTRODUCTION

In papermaking, internal sizing is the process of improving paper and paperboard with resistance to liquid wetting, penetration, and absorption by the use of sizing agents during sheet forming. Rosin with alum has been a dominant sizing agent for the process. In recent years, however, papermaking conditions have been rapidly shifting from acidic to neutral-alkaline regions for a variety of reasons. Under these conditions, conventional rosin sizing has become difficult to perform, partly because alum has a low cationicity at elevated pH and loses its ability to orient rosin size onto fiber surfaces. To solve this problem, polyamines have been used to substitute alum owing to their large cationic charge densities in the neutral pH region and large molecular weights.

In previous papers^[1, 2], we reported that the commercial rosin sizes with polyallylamine (PAAm), polyvinylamines (PVAm) and poly(dimethylamino ethylmethacrylate) (PDMAEMA) exhibit effective sizing in the pH region from 4 to 8, but their effectivenesses were quite different, and the sizing mechanism of the system is not clear. The purpose of the present study is to investigate the functions of the polyamines in neutral rosin sizing by means of X-ray photoelectron spectroscopy (XPS) and laser diffraction particle analysis.

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. PVAm and PDMAEMA were prepared based on the method of Tanaka and Senju^[3]. PAAm were obtained from Aldrich Co.. The average molecular weights of the polyamines were determined by size exclusion chromatography using poly(ethylene oxide) as standard polymer. The charge densities of the polyamines were

* This work was supported by International Co-operation Project of Fujian Province (99-I-5).

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Received July 12, 2000

analyzed by colloid titration with a potassium poly(vinyl sulfate) solution^[3]. The properties and molecular structures of the polyamines used in this study are shown in Table 1 and Fig. 1. PVAm has primary amino groups linked directly to the main chain. PAAm is also a primary amine, but has amino groups only in the side chains. PDMAEMA is a polymer having tertiary amino groups. The three polyamines (PVAm-1, PVAm-2 and PVAm-3) were used to examine the effects of the polyamine structures on the rosin sizing. The three polyvinylamines were designed to examine the effects of the molecular weights and charge densities of the polyamines on the rosin sizing.

Table 1. Effects of the properties of the polyamines on rosin sizing at pH 7.5

Polyamine	$M_w (\times 10^5)$	Charge density (mmol/g)	Sizing degree (s)	Rosin retention (%)
PAAm	5.7	8.0	17	79
PVAm-1	32.6	8.0	20	85
PVAm-2	3.6	8.2	18	82
PVAm-3	3.7	6.4	5	72
PDMAEMA	3.6	6.2	3	71

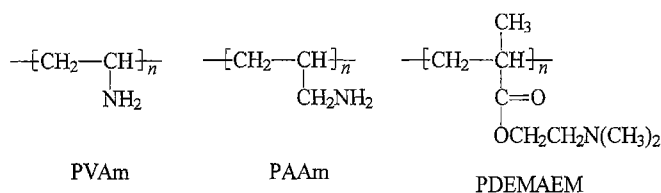


Fig.1 The molecular structures of the polyamines used in this study

Handsheet Preparation

The procedures for preparing rosin sizing followed the method described in the previous paper^[1]. The handsheets were prepared according to TAPPI Test Method T218-91. The sizing effectiveness was evaluated by the Stockigt test: A drop of 1% ferric chloride solution was applied to the upper surface of a sample folded for flotation. Immediately, the sample was floated on a 2% solution of ammonium thiocyanate. A sizing degree was evaluated by the time from the beginning of flotation to the development of a bright red color. Rosin retention by the polyamines was determined by extracting the handsheets with an acidified alcohol solution.

Size Measurement of RE-polyamine Complexes

The average sizes of RE-polyamine complexes were determined using a Shimadzu SALD-3000 laser diffraction particle analyzer. To 50 mL of an RE solution, a desired amount of the polyamine was added, and the mixture was stirred for 3 min. The solution was then added to the cell of the analyzer containing 400 mL of deionized water previously adjusted to pH 7.5 and mixed by a stirring propeller and a circulation pump. The measurement was carried out at 25°C.

XPS Measurements

The procedures for XPS analyses of polyamines on the surfaces of handsheets were based on the methods described by Chen and Tanaka^[4]. All XPS analyses were performed on a AXIS-His spectrometer (Shimadzu-Kratos Analytical) running at 15 kV-10 mA. Monochromatized AlK α radiation was used to excite the electrons. For all analyses, a low-energy electron flood gun was applied to neutralize the specimen surface. Gaussian curve fitting and quantification were performed using version 1.4.0 provided on the system. Binding energies of the spectra were related to C—C at 285.0 eV.

RESULTS AND DISCUSSION

Effects of Properties and Structures of the Polyamines

As shown in Table 1, the sizing of RE with any one of the five polyamines was effective at pH 7.5, but the charge densities and molecular weights (M_w) of the polyamines greatly influence sizing effectiveness. Although the MW

of PVAm-1 was about ten times higher than that of PVAm-2, and the two polyamines had the almost same charge densities, the sizing degree (20 s) of RE with PVAm-1 was only 2 seconds greater than that (18 s) of RE with PVAm-2. On the other hand, PVAm-2 and PVAm-3 had the almost same M_w , but the charge density (8.2 mmol/g) of PVAm-2 was larger than that (6.4 mmol/g) of PVAm-3. As a result of the difference in the charge densities, the sizing degrees of RE with PVAm-2 and PVAm-3 were 18 s and 5 s, respectively. The larger rosin retention by PVAm-2 (see Table 1) may be an explanation for the larger sizing degrees of RE with PVAm-2. These results indicate that the charge densities of the polyamines have a greater influence on the neutral rosin sizing than the MWs of the polyamines.

It is generally accepted that three basic requirements must be met to achieve effective sizing. (1) Rosin size must be retained on the fibers as much as possible; (2) the retained size must be distributed over fiber surfaces as evenly as possible, and (3) the retained size must be strongly bound to the fiber surfaces^[5-7]. The data in Table 1 shows that a larger sizing degree is related to a larger rosin retention, and the capacity of polyamines to retain RE is related to their charge densities and structures. The unit sizes of the polyamines increase in the sequence of PVAm-2 < PAAm < PDMAEMA, and PVAm-2 has the highest charge density among the three polyamines. As a result of the differences in the charge densities and the unit sizes, the sizing degrees of RE with the three polyamines decrease in the sequence of 18 s > 17 s > 3 s, and the rosin retention increases in the sequence of 82% > 79% > 71%. The previous papers^[1] have shown that the polyamines with linear structures are more effective than polyethyleneimine (PEI) with branched structure. It is evident that the polyamine with a larger charge density and a smaller unit size can retain more rosin size on fiber surfaces so that a better sizing effectiveness can be achieved.

Effect of Distribution of RE-polyamine Complexes

To investigate the distribution of rosin on the fiber surfaces, average sizes of RE-polyamine complexes were measured using a laser diffraction particle analyzer. The average colloidal particle size of RE is 304 nm. When polyamines were added to RE solutions, RE-polyamine complexes were formed, and the average sizes of the complexes increased as the amounts and the unit sizes of the polyamines were increased (Fig. 2). At a weight ratio 1:1 for polyamine to RE, the average sizes of the complexes of RE with PVAm-2, PAAm, and PDMAEMA are 377, 385, and 414 nm, respectively. These results indicate that a linear polyamine having smaller side chains can form smaller RE-polyamine complexes so that it can cover larger fiber surfaces at a given rosin retention. This meets with the basic requirement that retained rosin must be distributed over fiber surfaces as evenly as possible.

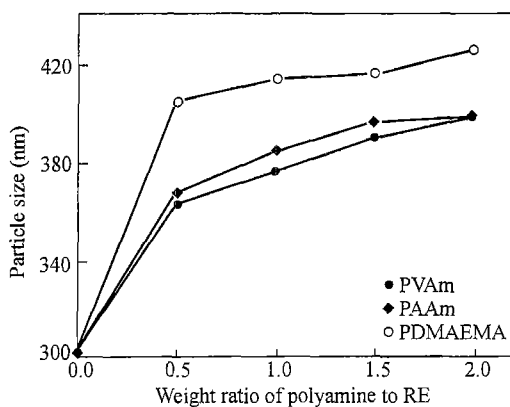


Fig. 2 Average sizes of RE-polyamine complexes at pH 7.5

Bonding of the Polyamines on Fiber Surfaces

To clarify the bonding forms of RE with the polyamines on the fiber surfaces, surface characterization of the handsheets sized with RE and the polyamines was carried out by using XPS. Figure 3(a) is the XPS N1s

spectrum of PAAm heated at 105°C for 10 min. There are two signals in the spectrum, N4 at 401.4 eV may originate from ammonium groups (NH_3^+), and N2 at 399.3 eV may be assigned to amino groups in PAAm. Figure 3(b) is a XPS spectrum of the handsheet bonded with PAAm only. The handsheet was formed by adding PAAm to pulp suspension, filtering and heating the wet fibers at 105°C for 10 min. There are three peaks in Fig. 3(b), N1 (399.3 eV), N2 (400.0 eV, $\text{CONH}-$), and N4 (401.4 eV). On comparing Fig. 3(a) and Fig. 3(b), their difference indicates that about 30% of the nitrogen atoms in PAAm reacted with the carboxyl groups of the fibers to form amide bonds.

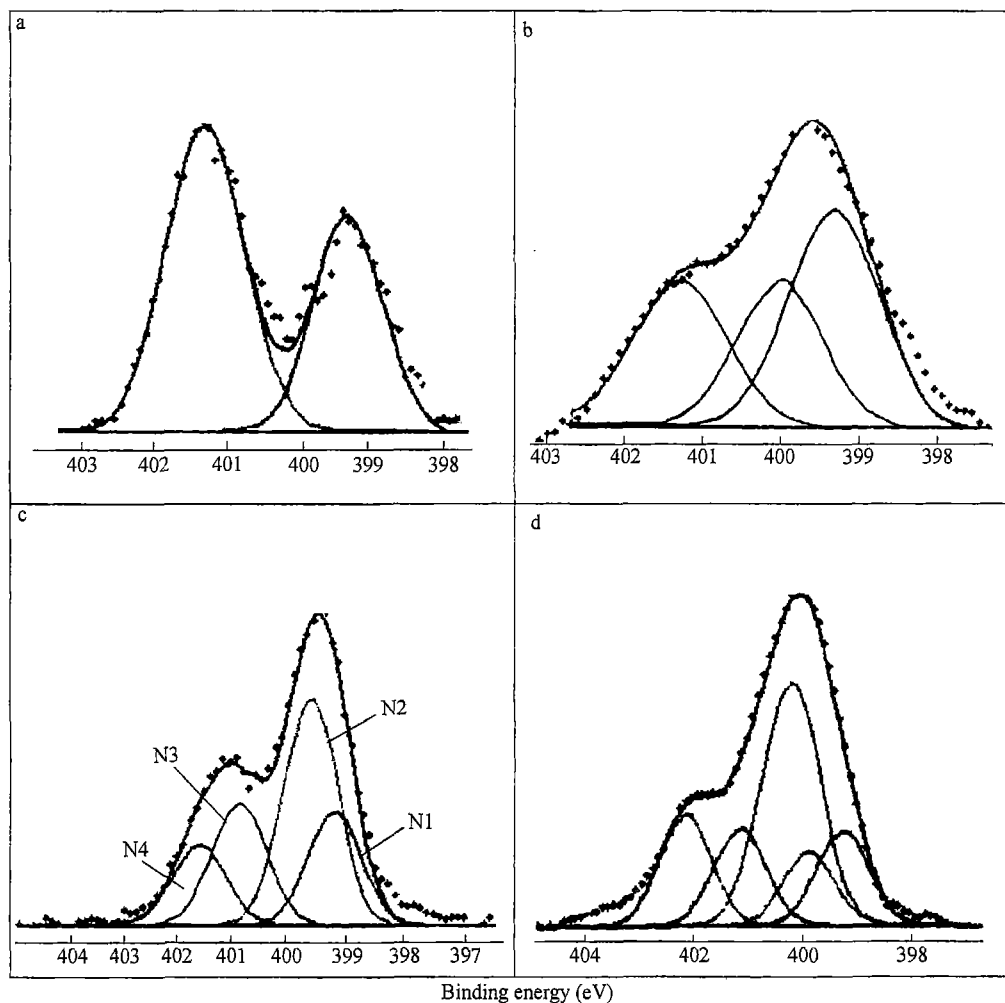


Fig. 3 XPS N1s spectra of PAAm and the sheets

- a) PAAm heated at 105°C for 10 min
- b) Sheet added with PAAm
- c) Sheet sized with RE and PAAm
- d) Sheet sized with RE and PDMAEMA

A new peak N3 at 400.7 eV appears in the XPS spectrum of the sheet sized with RE and PAAm (Fig. 3c). On the basis of the binding energy^[8], the signal may be assigned to the $-\text{OC}-\text{N}-\text{CO}-$ structure formed between RE and PAAm. N3 at 400.6 eV is also present in the spectrum of the sheet sized with RE and PVAm, but N3 can not be found in the spectrum of the sheet sized with RE and PDMAEMA (Fig. 3d). This means that PDMAEMA can not react with RE to form the $-\text{OC}-\text{N}-\text{CO}-$ structure so that the retained rosin can not be bound to the fiber surfaces as strongly as PVAm-2 and PAAm are. Since the sizing degree of RE with

PDMAEMA is very small (3 s), these results, therefore, suggest that the formation of the —OC—N—CO— structure between the amino groups of the polyamines and the carboxyl groups of the fibers may be a key step for effective rosin sizing.

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