Effects of Polyamine Structure on Rosin Sizing Under Neutral Papermaking Conditions

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ABSTRACT: The sizing effectiveness of rosin size with four typical polyamines, polyvinylamine (PVAm), polyallylamine (PAAm), poly(dimethylamino ethyl methacrylate) (PDMAEMA), and polyethyleneimine (PEI), was investigated under neutral papermaking conditions. The polyamines with linear structures were more effective than was PEI with a branched structure. The smaller the side chains of the linear polyamine, the larger was the sizing degree of the rosin emulsion size (RE) with the polyamine. The polyamine with smaller molecular geometric size could retain more rosin size on the pulp and form smaller rosin–polyamine complexes. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 2159–2163, 1997

Key words: neutral papermaking; sizing; rosin; polyamines; molecular structure

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 sheet forming. Rosin with alum has been a dominant sizing agent since 1807. The rosin sizing agent is obtained in two forms: a sodium or potassium salt solution of rosin acids (soap size) and an emulsion of the rosin acids (emulsion size). Emulsion size can be used at a slightly higher pH, up to pH 6.5, than the level of pH 4–6 used for the soap size. In the recent years, however, papermaking conditions have been rapidly shifting from acidic to neutral–alkaline regions due to the greater use of calcium carbonate, the greater extent of the white water system closure, and so forth. Under these conditions, conventional rosin sizing has become difficult, partly because alum has a low cationicity at elevated pH's and loses its ability to orient rosin size onto pulp surfaces.[1–3]

Many chemicals have been tested to improve the cationicity of alum at higher pH's so that rosin sizing can be applied to neutral papermaking systems.[4–9] Among these chemicals, polyamines are attracting considerable attention because of their large cationic charge densities in the neutral pH region and high molecular weights.[7–9] In a previous article,[10] we reported that four commercial rosin sizes with a typical polyamine, polyvinylamine (PVAm), exhibited effective sizing in the pH region from 4 to 8. This article deals with the effects of polyamine structure on rosin sizing under neutral papermaking conditions. The effectiveness in sizing of a emulsion size and a rosin soap size with four typical polyamines, namely, PVAm, polyallylamine (PAAm), poly(dimethylaminoethyl methacrylate) (PDMAEMA), and polyethyleneimine (PEI), were investigated at pH's from 4 to 8. The structures are shown in Figure 1. The effects of the size retention by the polyamines, the charge densities of the polyamines, and the particle sizes of rosin–polyamine complexes on the degree of sizing were examined.

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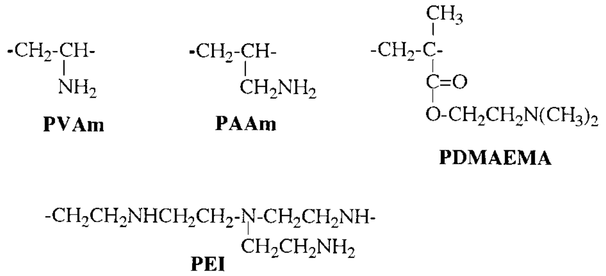

$-CH_2-CH(NH_2)-$

PVAm

$-CH_2-CH(CH_2NH_2)-$

PAAm

$-CH_2-C(CH_3)(C{=}O\text{-}O\text{-}CH_2CH_2N(CH_3)_2)-$

PDMAEMA

$-CH_2CH_2NHCH_2CH_2-N(CH_2CH_2NH_2)-CH_2CH_2NH-$

PEI

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

EXPERIMENTAL

Materials

A commercial bleached hardwood kraft pulp was used. The pulp was beaten to a Canadian Standard Freeness (CSF) of 409 mL in a TAPPI standard beater. A rosin emulsion size (RE) and a rosin soap size (RS) were obtained from a size manufacturer. PVAm was prepared based on the method of Tanaka and Senju.[11,12] The average molecular weight was 36,000 according to size exclusion chromatography[13,14] using poly(ethylene oxide)s (Tosoh Co., Japan) as standard polymers. PAAm (with an average molecular weight of 53,000) was obtained from Aldrich Co. PEI and PDMAEMA were purchased from Tokyo Kasei Kogyo Co. and had average molecular weights of 57,000 and 45,000, respectively. The cationic charge densities of the polyamines were determined by colloid titration with a $10^{-4}N$ standard solution of potassium poly(vinyl sulfate).[11] The molecular structures of these polyamines are shown in Figure 1.

Measurement of Particle Sizes of RE–Polyamine Complexes

The particle sizes of RE–polyamine complexes were determined using a Shimadzu SALD-3000 laser diffraction particle-size analyzer. To 50 mL of an RE solution (pH 7.5, at consistency of 0.024%), the desired amount of the polyamine was added, and the mixture was stirred for 3 min. The solution was then added to the tank 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.

Sizing Procedures

Handsheets with a basis weight of about 60 g/m^2 were formed according to the TAPPI Test Method T205om-88. The sizing effectiveness of RE and RS with the polyamines was evaluated by the Stöckigt test (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. Size retention by the polyamines was determined by the amount of rosin size extracted from the papers with an acidulated alcohol solution.[15]

RESULTS AND DISCUSSION

Sizing Effectivenesses of the Rosin Sizes with the Polyamines

Figure 2 shows the sizing effectiveness of the RE with the four polyamines at different pH's. For comparison, the sizing results with RE and alum are also shown in Figure 2. It can be seen that RE with alum at pH 4 exhibited a greater sizing effectiveness than did RE with polyamine. The degree of sizing of RE with alum at pH 4 was 37 s, while that of RE with the four polyamines was 28, 27, 23, and 15 s, respectively. The sizing of

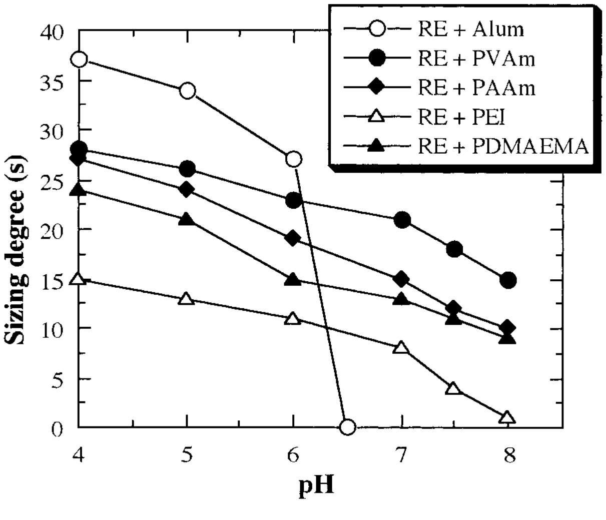

Figure 2 Effects of sheet-forming pH on sizing effectiveness of RE with the polyamines. The amount of RE, the polyamines, and alum added were 5, 10, and 20 mg/g pulp, respectively.

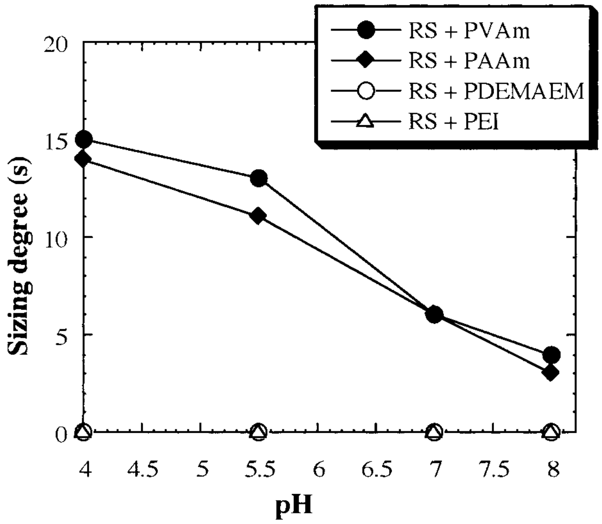

Figure 3 Effects of sheet-forming pH on sizing effectiveness of RS with the polyamines.

RE with alum became ineffective at pH 6.5, although RE with the polyamines still performed well at pH 7. These results illustrate that the sizing of RE with any one of the four polyamines is effective at neutral pH.

Figure 3 shows the sizing degree of the RS with the polyamines as a function of the sheet-forming pH value. The sizing with RS and PDMAEMA and PEI was not developed at all in the region from pH 4 to 8. RS with PVAm and PAAm showed effective sizing to some extent at pH's from 4 to 6, but the degree of sizing of RS with PVAm and PAAm at pH 8 was only 4 and 3 s, respectively. These results indicate that the polyamines are not a suitable aid for a RS under neutral papermaking conditions. For this reason, the following discussion deals only with the effects of the polyamine structure on the sizing of RE with the polyamines.

Effects of Polyamine Structure on the Sizing

The sizing results demonstrate that, although RE with one of the four polyamines gave effective sizing in the region from pH 4 to 8, the degree of sizing was quite different from one polyamine to another. This implies that the polyamine structure greatly influences its efficiency in rosin sizing. It is generally accepted that the functions of a polyelectrolyte are determined mainly by its molecular weight, its charge density, and molecular geometric structures. The average molecular weights of the four polyamines used in this study covered the region from 36,000 to 57,000, i.e., the differences of molecular weights of the polyamines were small. Our previous work[10] illustrated that such small differences have little effect on neutral rosin sizing.

Figure 4 shows the charge densities of the polyamines determined by titration with a $10^{-4}N$ potassium poly(vinyl sulfate) solution as a function of pH. The charge density of PEI is higher than that of the other three polyamines over the pH region from 4 to 8. PVAm has almost the same charge density as that of PAAm at pH 4–5. However, the degree of sizing of RE with the polyamines shown in Figure 2 demonstrates that RE with PEI gave the smallest degree of sizing among the four polyamines and that the sizing with RE and PVAm was more effective than with RE and PAAm. There is no clear relationship between the cationic charge density of the polyamines and the sizing degree.

On the other hand, 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 chain. PDMAEMA is a polymer having tertiary amino groups. These three polyamines are linear structures. PEI has a branched structure and contains primary, secondary, and tertiary amino groups in a ratio of approximately 1 : 2 : 1.[16] The molecular geometric sizes of the linear polyamines increase in the sequence PVAm < PAAm < PDMAEMA, as shown in Figure 1. This sequence agrees well with their sizing degree sequence, as shown in Figure 2. The larger the side chains of the polyamines, the smaller the siz-

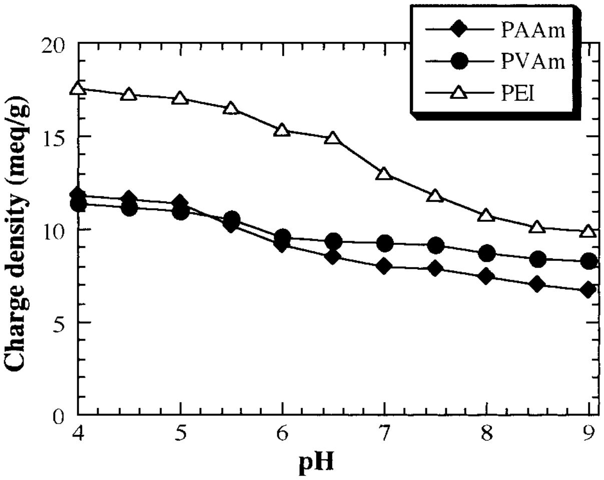

Figure 4 Effect of pH on the cationic charge density of the polyamines.

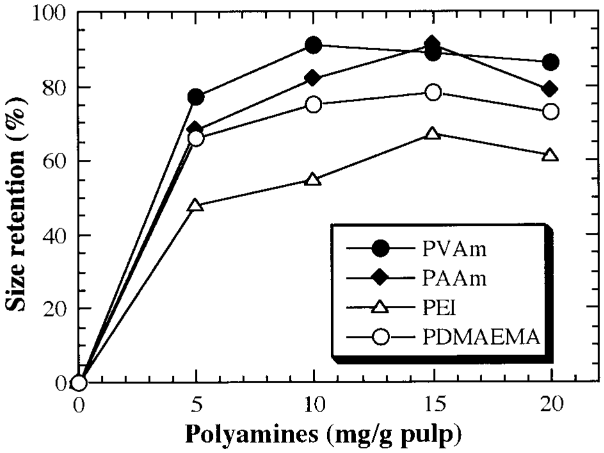

Figure 5 Retention of RE on the pulp in the presence of the polyamines at pH 7.5.

ing degrees with RE. The sizing effectiveness of RE with PEI having a branched structure was smaller than that of RE with the three linear polyamines. These results illustrate that the molecular geometric size of the polyamines has a great influence on the neutral rosin sizing. One possible explanation for these results may be that the polyamine having a smaller molecular geometric size forms a smaller size-polyamine complex as described below.

Effects of Polyamine Structure on the Size Retention

The numerous studies$^{1-3}$ on the mechanisms of rosin sizing in the past century reached an agreement that three basic requirements must be met to achieve effective sizing, viz., (1) rosin size must be retained on the fibers as much as possible, (2) the retained size must be distributed over all fiber surfaces, and (3) the retained size must be strongly bound to the fiber surfaces. Figure 5 shows the retention of RE on the pulp with the four polyamines as a function of the added amount at pH 7.5. The size retention increased with an increasing amount of the polyamines and leveled off at about 10 mg/g pulp. At each level of addition, the capacity of the polyamines to retain RE on the pulp decreased in the sequence PVAm $\geqq$ PAAm > PDMAEMA > PEI. This is consistent with the sequence of the sizing degree with RE and the same amount of the polyamines, as shown in Figure 2. It thus became clear that a polyamine with a smaller molecular geometric size can retain more rosin size on pulps at a given amount so that a better sizing effectiveness can be achieved.

Effect of Polyamine Structure on Particle Sizes of RE–Polyamine Complexes

Figure 6 shows the average particle size of RE–polyamine complexes in aqueous solutions at pH 7.5. The average particle size of RE was 304 nm. When polyamines were added to RE solutions, RE–polyamine complexes were formed, and the average particle sizes of the complexes increased as the amounts of the added polyamines were increased. When the weight ratio of the polyamine to RE was 1 : 1, the sizes of the complexes of RE with PVAm, PAAm, and PDMAEMA were 377, 385, and 414 nm, respectively. This indicates that the polyamine having the smaller side chains forms a smaller RE–polyamine complex which can cover a larger pulp surface area at a given size retention. Good size retention and an even distribution of retained size are, as has already been mentioned, the basic requirements for effective rosin sizing. A polyamine with smaller side chains can retain more rosin size and form smaller complexes of rosin size–polyamine, which means that it can perform better in a neutral rosin sizing than can a polyamine having larger side chains.

The average particle size of the RE–PEI com-

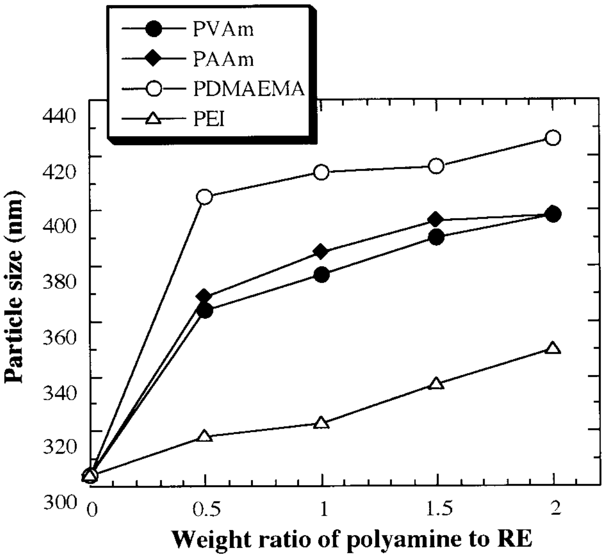

Figure 6 Particle size of RE–polyamine complexes in aqueous solutions at pH 7.5. The consistency of RE was 0.024%.

plex was the smallest of the four polyamines, and the retention of RE by PEI was also the smallest of the four polyamines, as shown in Figure 5. Since the PEI was the least effective of the four polyamines (Fig. 2), retention of rosin size by the polyamines seem to be more important than is the average particle size of the rosin size–polyamine complex.

CONCLUSIONS

Rosin emulsion size (RE) with four typical polyamines, polyvinylamine (PVAm), polyallylamine (PAAm), poly(dimethylaminoethyl methacrylate) (PDMAEMA), and polyethyleneimine (PEI), exhibited effective sizing under neutral papermaking conditions. The structure of the polyamine greatly influences its efficiency in the rosin sizing. The polyamines with linear structures were more effective than was PEI with a branched structure. Among the three linear polyamines, the smaller the side chains of the polyamines, the larger was the retention of RE by the polyamines, and the smaller the average particle size of the RE–polyamine complex, the larger was the sizing degree of RE with the polyamines under neutral papermaking conditions.

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