Vinylformamide-based cationic polymers as retention aids in alkaline papermaking

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ABSTRACT: With papermaking processes shifting from acidic to alkaline conditions, researchers are studying methods to improve sizing under alkaline conditions, including the use of novel retention aids. In this study, vinylformamide-based cationic polymers were synthesized and were characterized with GPC and polyelectrolyte titration. The polymers were then used as retention aids for rosin size under alkaline conditions. The polymers showed great potential as retention aids, with the performance of each being relative to the chemical structure of its cationic portion and its molecular weight. Furthermore, the characterization of the retention behavior by SEM and ESCA revealed that the polymer molecules could physically form a special structure with rosin size particles so that the rosin size particles would still be stable under alkaline conditions.

Application: Paper mills can use the new cationic polymers as effective retention aids with conventional rosin sizes in alkaline papermaking.

In recent years, papermaking technology has been rapidly shifting from acidic to neutral and alkaline conditions. As a result, papermakers have moved away from traditional rosin–alum sizing systems to the use of neutral rosin size and to the use of synthetic sizes such as alkyl ketene dimers (AKD) and alkenyl succinic anhydrides (ASA). However, the traditional sizing agents, including acidic emulsion rosin size and rosin soap size, are inexpensive and easy to prepare, and it would be economically attractive to apply them to neutral or alkaline paper sizing.

Researchers have explored new types of rosin size as well as some novel retention systems in efforts to find an effective way to utilize conventional acidic rosin sizes in alkaline papermaking [1–4]. A number of chemicals have been tried as retention aids either in combination with alum or as alum substitutes [5–10]. Of these chemicals, many cationic polymers have been found to be promising.

Cationic polymers like polyamines and cationic polyacrylamide are used frequently in paper manufacturing as strength additives, flocculants, and retention aids. Recently, they have also been applied in neutral or alkaline paper sizing as mordants or retention aids for rosin size [9]. Some polymers have been shown to have high performance in rosin–alum sizing over pH values ranging from pH 4 to pH 8 [11]. Furthermore, a very small amount of polymer can greatly decrease alum dosage and increase the sizing efficiency of rosin–alum sizing under neutral or alkaline conditions [12]. Since the polymers function as paper strength agents too, a sizing system consisting of rosin size, alum, and polymer can also increase the paper strength.

As our previous research indicated, a cationic poly-*N*-vinylformamide was effective as a co-retention aid in alkaline paper sizing with rosin size and would improve the stability of both the rosin size particles and the cationic aluminum complexes under alkaline conditions [13, 14]. As the work continued, we synthesized (a) aminated poly-*N*-vinylformamides and (b) copolymers of vinylformamide and different quaternary ammonium cationic monomers. We have now applied these polymers as retention aids in alkaline paper sizing with acidic emulsion rosin size. We have also used SEM and ESCA techniques to investigate the interaction mechanisms of the polymers with rosin size particles. Here, we report on our findings.

EXPERIMENTAL

Materials

N-vinylformamide (Aldrich) was distilled under reduced pressure prior to polymerization. We purified (2-methacryloyloxy) ethyl trimethyl ammonium chloride (MATMAC, from Aldrich) by passing it through an inhibitor remover column. We used 2,2´-azobis (2-amidinopropane) dihydrochloride (AADPC) as received (from Waco) for an initiator to start the radical polymerization.

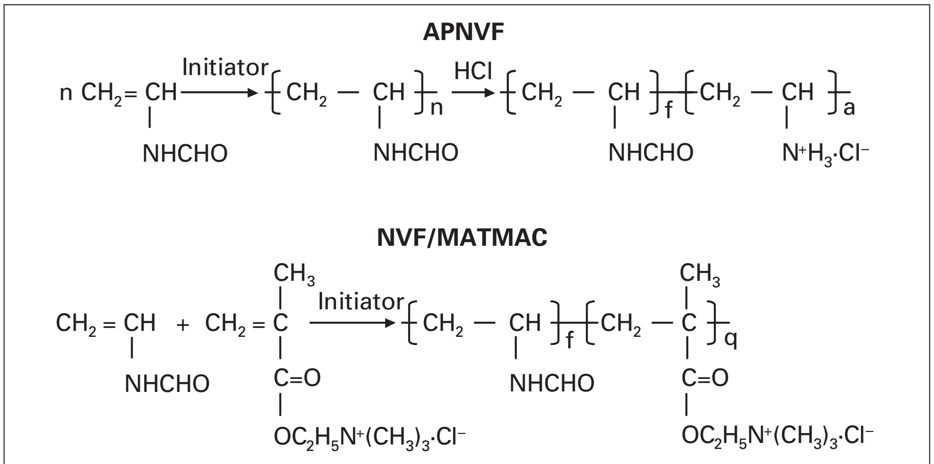
A commercial hardwood bleached kraft pulp beaten to 380 mL CSF was used for making handsheets. An acidic emulsion rosin size prepared in the laboratory was used as the sizing agent. An analytical grade of alum (Waco) was used as the retention aid, and poly diallyldimethyl ammonium chloride (Aldrich) was used as a reference co-retention aid.

Synthesis of polymers

All of the radical polymerizations were conducted under identical experimental conditions. Aminated poly-*N*-vinylformamides (APNVF) were synthesized by partly hydrolyzing polymerized NVF with concentrated HCl [15]. Copolymers of NVF with MATMAC were synthesized by direct copolymerization of the two monomers in water.

For the polymerization, all materials except initiator were first added to a 200-mL flask fitted with a mechanical stirrer, a water-cooled reflux condenser, and a nitrogen inlet. The flask was immersed in a thermostatically controlled water bath. The solution was flashed with nitrogen at ambient temperature for 1 h under an agitation of 250 rpm. The water bath was then heated and kept constant at 60°C. Finally, dissolved initiator was added, and the reaction was carried out under nitrogen for 6 h.

We precipitated the resulting polymers by pouring the solution into isopropanol, purifying the polymers with repeated precipitations. After the purified polymers were dried under vacuum, a measured amount was dissolved in distilled water and diluted to a concentration of 0.05%. There was no other treatment prior to use.



1. HCl is used to hydrolyze poly-NVF to aminated poly-NVF, and an initiator is used to bring about the copolymerization of NVF with MATMAC.

	AAPDC,* mmol	MOLECULAR WEIGHT	PERCENTAGES, *a/f* or *q/f*	CHARGE DENSITY, meq/g
APNVF				
1	0.012	$2.60 \cdot 10^6$	15 – 85	2.10
2	0.018	$1.72 \cdot 10^6$	19 – 81	2.76
3	0.037	$1.31 \cdot 10^6$	17 – 83	2.38
4	0.050	$8.85 \cdot 10^5$	21 – 79	2.86
5	0.075	$3.71 \cdot 10^5$	20 – 80	2.78
NVF/MATMAC				
1	0.025	$1.56 \cdot 10^6$	8.9 – 91.2	1.16
2	0.050	$0.61 \cdot 10^6$	10.2 – 89.8	1.20
3	0.200	$0.41 \cdot 10^6$	10.7 – 89.3	1.25

*2,2´-azobis (2-amidinopropane) dihydrochloride.

I. Characteristic parameters of APNVF (a/f values) and NVF/MATMAC (q/f values).

Preparation of handsheets

A pulp suspension of 1.2% consistency was first adjusted to the assigned pH with 0.1 mol/L HCl or NaOH solution under stirring. Alum solution was added, followed by rosin emulsion and polymer. The pulp stock was adjusted again to the desired pH with dilute HCl or NaOH and was allowed to stand for 1 min under moderate stirring.

Handsheets with a basis weight of 60 g/m^2 were made according to TAPPI T 205 om-88. Wet sheets were pressed at 0.35 MPa for 5 min. Part of handsheets were dried in a convection oven at 105°C for 10 min and were conditioned at 23°C and 50% RH for more than 24 h. Another part of the handsheets, to be used for SEM work, were freeze-dried for more than 12 h.

Analytical methods

The molecular weights of the polymers were determined by gel penetration chromatography (GPC) [16–17], and the cationic charges of the polymers were determined by polyelectrolyte titration, with acriflavine hydrochloride as a fluorescent indicator [18, 19]. The degree of sizing of each handsheet was determined by the Stöckigt test (JIS P8122). The amount of rosin size retained in handsheets was determined by the pyrolysis–GC method, in which tetramethylammonium hydroxide was used as a methylating agent for the carboxyl group [20].

For SEM measurements, the paper samples were first coated with gold and then examined with the scanning electron microscope in a high vacuum mode. We used a commercial X-ray photoelectron spectrometer to make ESCA (electron spectroscopy for chemical analysis) measurements of the polymer films with rosin size.

RESULTS AND DISCUSSION

Characteristics of the polymers

The chemical structures and charge densities of cationic polymers used as retention aids greatly influence the sizing efficiency of rosin sizes [9, 14, 21]. Both APNVF and NVF/MATMAC have an formamido group (-NHCHO), as shown in **Fig. 1**. In addition, APNVF has an amino group ($-N^+H_3 \bullet Cl^-$), while NVF/MATMAC has a quaternary ammonium group ($-OC_2H_5N^+(CH_3)_3 \bullet Cl^-$). In having these functional groups, the polymers differ from polyvinylamine (PVA), polyallylamine (PAA), and polyethyleneimine (PEI), which have been tested as retention aids for neutral or alkaline rosin sizing.

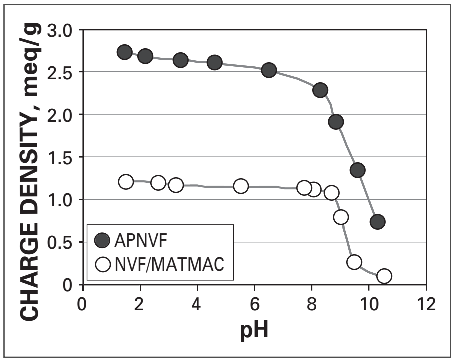
The formamido group in the polymer structure is considered effective for the retention of rosin size particles [14]. **Table I** shows the characteristic parameters of APNVFs 1–5 and the NVF/MATMAC copolymers. We calculated the percentages for amino and formamide groups in the APNVFs and for the quaternary ammonium and formamido groups in the NVF/MATMAC copolymers according to their cationic charge densities as determined by polyelectrolyte titration at pH 2.0 [22].

Figure 2 shows that the two polymers differ in the way their charge densities change. The charge density of APNVF decreased slightly with increasing pH up to 8.5 and decreased quickly afterwards. By contrast, the charge density of NVF/MATMAC almost did not decrease at all before pH 8.5 but decreased very quickly when the pH was over 8.5. The sharp decrease in the charge density of the polymer NVF/MATMAC is probably caused by the cleavage of the ester bond between the main chain and the cationic quaternary ammonium group.

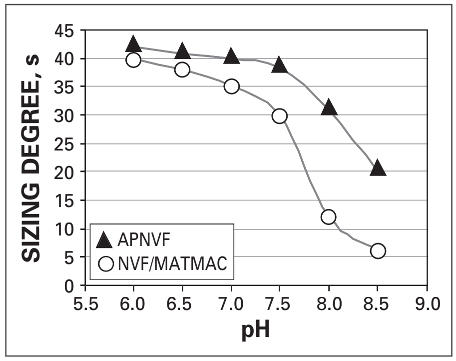
Even up to pH 10, both APNVF and NVF/MATMAC are still cationic, as the curves in the figure show. This feature is important to the adsorption of polymer onto pulp fibers and the retention of anionic rosin size particles on fiber surfaces under alkaline conditions.

Sizing efficiency

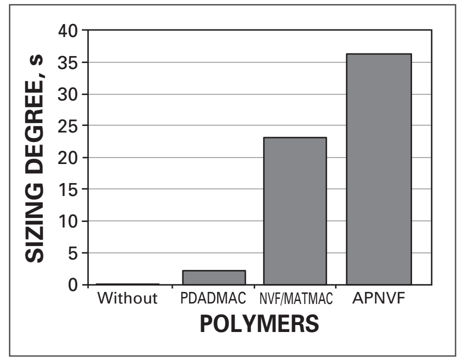
Figure 3 shows the sizing efficiency of the acidic emulsion rosin size with alum as retention aid and cationic polymer as co-retention aid under weak acidic to alkaline conditions. Alum cannot be used as an effective retention aid for rosin size under neutral–alkaline conditions without other co-retention aids like cationic polymers. However, the sizing results shown in Fig. 3 indicate that good sizing of paper with acidic rosin size and alum is achieved when only 0.1% cationic poly-



2. Variation in charge density variation with pH for the aminated poly-NVF and the copolymer NVF with MATMAC .



3. Degree of sizing from pH 6.0 to pH 8.5. APNVF was more efficient than NVF/MATMAC as a co-retention aid under alkaline conditions.



4. Comparison of sizing efficiency between APNVF, NVF/MATMAC, and poly-DADMAC as a reference.

mer APNVF or NVF/MATMAC is used as a co-retention aid over a wide range of pH up to 8.5.

Apparently, both APNVF and NVF/MATMAC are effective retention aids in sizing paper with rosin size. On the other hand, we expected that the difference in the charge density variation of the two polymers as the function of pH would induce performances in sizing. Figure 3 shows that APNVF was more efficient than NVF/MATMAC as a co-retention aid under alkaline conditions. The poor retention effect of NVF/MATMAC on rosin size at pH over 8.5 is thought to be attributable to the decomposition of the polymer molecules (the cleavage of the ester bond).

To evaluate the performance of the two vinylformamide-based cationic polymers, we compared the two with a reference cationic polymer, poly-DADMAC. The results are shown in **Fig. 4**. When the paper was sized with rosin size and alum but without polymer at pH 7.8, there was no sizing effect. The addition of poly-DADMAC as co-retention aid seldom gave paper sizing. However, when we added NVF/MATMAC and APNVF as co-retention aids, we obtained good sizing of paper. Consequently, the good performance of these two cationic polymers in sizing appears to correlate with their chemical structures.

Influence of polymer molecular weight

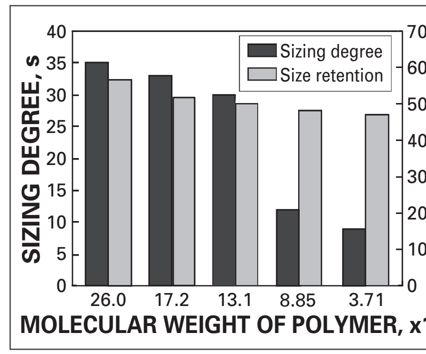
Molecular weight is one of the important characteristics of polymers. Pulp fibers are porous material, and this porosity may influence the adsorption of polymer molecules on the fiber surface. The molecular weight of the polymer plays an important role in the decay of the surface charge of pulp fibers [23, 24]. To explain the phenomenon of charge decay, it has been proposed that polymer molecules penetrate the pores of the fiber surface [25].

However, how does the molecular weight of the polymer influence the rosin sizing when the polymer is used as a co-retention aid? To explore this question, we synthesized APNVFs with different molecular weights and used them as co-retention aids in this study.

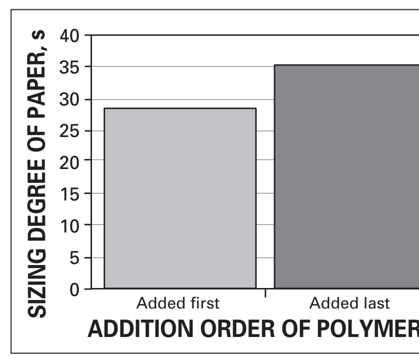
Figure 5 shows the results of sizing paper with the emulsion rosin size, alum, and APNVFs of different molecular weights. The degree of sizing decreased with the decrease in molecular weight of the APNVF, although the size retention did not follow the same trend. The figure also shows that the sizing of paper sharply decreased when the molecular weight of the APNVF was lower than 10^6. The polymer NVF/MATMAC had the same performance as well (not shown). These results suggest that the polymer molecular weight influenced the sizing performance significantly and that the polymer should have a minimum molecular weight to be used effectively as a retention aid.

The effect of the molecular weight on sizing is probably explained by the penetration of polymer molecules into the pores of pulp fibers. The polymer molecules with low molecular weights migrate easily into the pores of pulp fibers once they have absorbed onto the fiber surface. As a result, their orientation function on the rosin size would be lost.

If the phenomenon is really attributable to the penetration of polymer molecules into the pores of fibers, then the order in which polymer is added must also influence the sizing performance. To confirm this hypothesis, we carried out

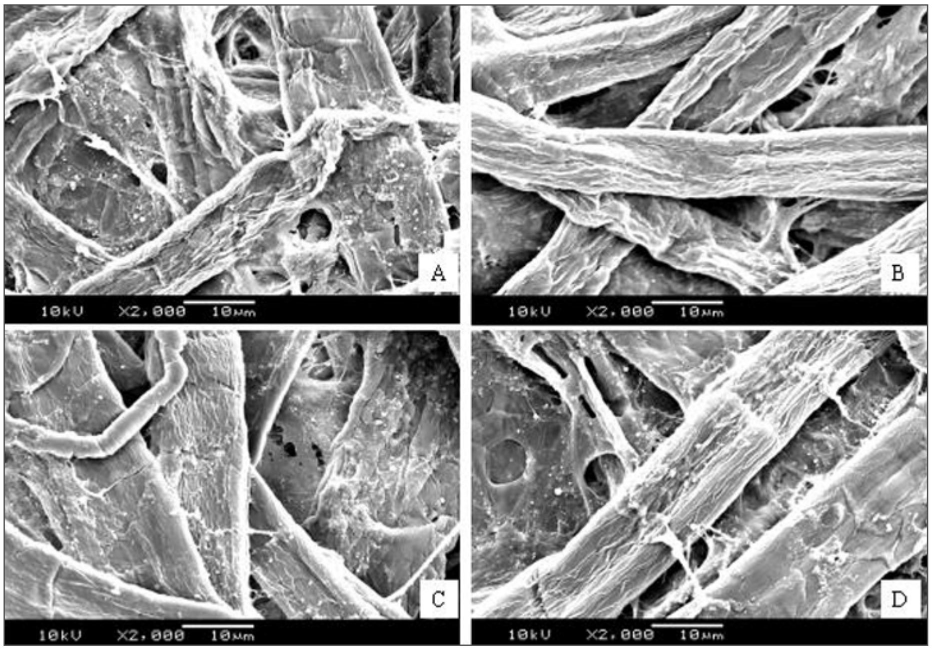


5. Sizing efficiency and retention for APNVF at different molecular weights.

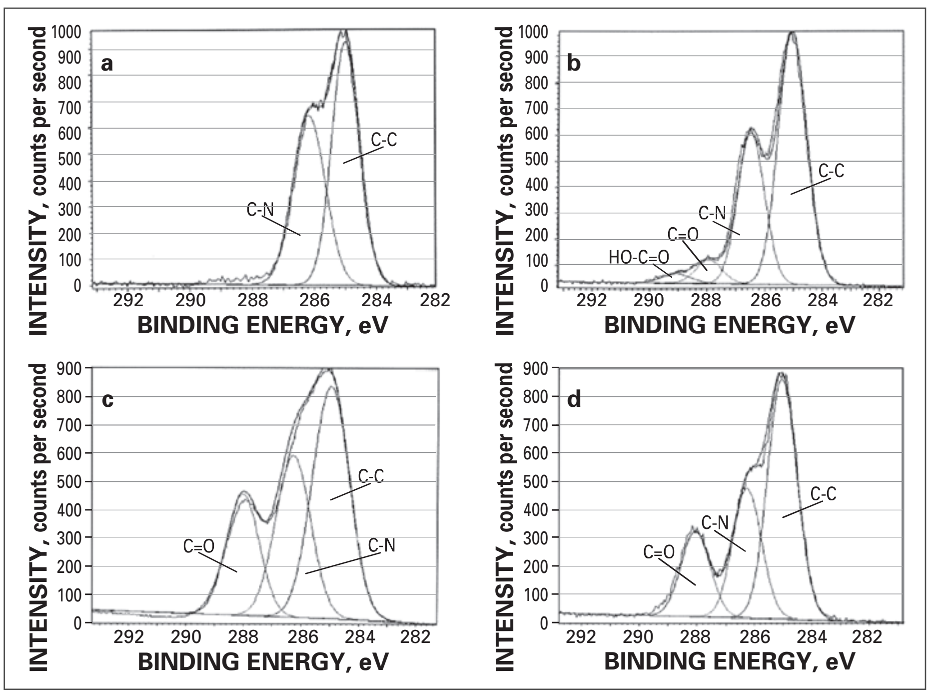


6. Sizing efficiency when APNVF was added first and when APNVF was added last.

experiments in which we changed the addition order. In one trial, APNVF was added to the fiber suspension before alum and rosin size; in another trial, APNVF was added just after alum and rosin size. The sizing results are illustrated in **Fig. 6**. As expected, the degree of sizing was higher when APNVF was added last than when it was added first. The polymer molecules have more chance to penetrate into fiber pores when the polymer is added first. This finding confirms that hypothesis that the effect of polymer molecular



7. SEM images showing fiber surfaces when sizing was conducted (A) at pH 5.5 without the addition of polymer added, (B) at pH 7.8 without polymer, (C) at pH 7.8 with NVF/MATMAC added, and (D) at pH 7.8 with APNVF added.



8. ESCA spectra of (a) poly-DADMAC, (b) the mixture of poly-DADMAC and rosin size, (c) the polymer APNVF, and (d) the mixture of APNVF and rosin size.

weight on sizing is the result of the pore-penetration behavior of the polymer.

Interaction mechanism of polymer and rosin size

Our previous study indicated that the effective cationic polymers could improve the stability of both the rosin size particles and cationic aluminum complexes under alkaline conditions [14]. The particles of acidic emulsion rosin size will dissociate as a result of the action of hydroxyl ion under alkaline conditions if an effective cationic polymer is not added. On the other hand, alum will lose its cationic properties because of its further hydrolysis under alkaline conditions. However, our previous study confirmed that the rosin size particles would still be stable and that the aluminum complexes still had cationic properties under alkaline conditions when some effective polymers were added [14]. Therefore, the polymer molecules are assumed to have some special interactions with the rosin size particles and aluminum complexes. Consequently, we wanted to examine and clarify the mechanism by which polymer and rosin size interact. To do so, we used SEM and ESCA techniques.

SEM. **Figure 7** shows the SEM image of the fiber surfaces of the paper sized with the rosin size and alum with or without the cationic polymer. Alum retained the rosin size particles on the fiber surfaces when the sizing was conducted under acidic conditions (pH 5.5) even without the addition of polymer (Frame A). However, no size particles were adsorbed on the fiber surfaces when the paper was sized with rosin size and alum without polymer at pH 7.8 (Frame B). This outcome suggests that the rosin size particles were stable at pH 5.5 but were dissolved at pH 7.8.

However, when NVF/MATMAC or APNVF was added (at 0.1% based on pulp) as a retention aid with alum in sizing at pH 7.8, the rosin size particles that adsorbed on the paper surface were clearly observed (Fig. 8, Frames C and D, respectively). The papers had good sizing in Cases A, C, and D but no sizing in the Case B. These results suggest that the stability of the size particles is essential for good sizing with the emulsion rosin size and that one of the important functions of the cationic polymer in alkaline rosin sizing is to improve the stability of size particles. The results also indicated that the polymers APNVF and NVF/MATMAC could effectively prevent the de-emulsification and dissociation of emulsion rosin size particles as a result of the action of OH^-.

ESCA. ESCA has been successfully used for the chemical analysis of solid surfaces, including films, paper sheets, and metal. Since the photoelectrons generated from the specimen by the X-ray radiation can penetrate to a thickness of only about 10 nm, ESCA is primarily useful in the chemical analysis of the outermost layer of solid samples. In our study, we used this technique to evaluate the interaction of the cationic polymer molecules with rosin size particles.

Figure 8 shows the ESCA C1s spectra of the samples. Poly-DADMAC had no retention effect on the emulsion rosin size, and its addition did not yield good paper sizing, indicating that poly-DADMAC molecules cannot interact with or cover the rosin size particles to prevent them from dissociating (because of the action of OH^- under alkaline conditions).

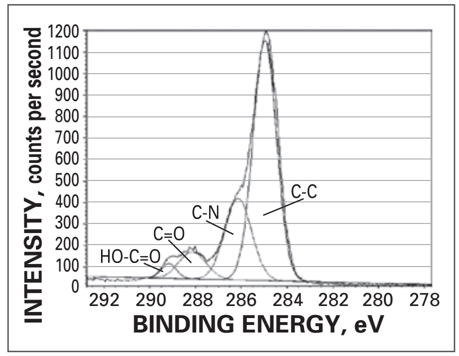
As expected, the ESCA C1s spectra of poly-DADMAC (Fig. 8a) and the mixture of poly-DADMAC with rosin size (8b) indicated that the rosin size particles were not covered by the polymer molecules but were randomly distributed. Hence, in Fig. 8b, we have the peak at a binding energy of 289.18 eV, which is assigned to the HO-C=O of the rosin acid. However, the ESCA C1s spectra of the mixture of APNVF and the rosin size (d) were the same as those of the polymer APNVF (c). The peaks at binding energies 285 eV, 286.3 eV, and 288.2 eV are assigned to the C–C, C–N and C=O of the polymer APNVF, respectively. Interestingly, the peak at 289.2 eV generated from the carboxyl group of rosin acid disappeared in the spectra of the mixture of APNVF and rosin size (Fig. 8d).

Where were the rosin size particles? The suitable explanation is that the surfaces of the rosin size particles were covered well by the long-chain APNVF molecules, probably forming a polymer molecule layer. As a result, the photoelectron signal generated from the rosin composition would have been weaken, and the ESCA equipment may have had difficulty detecting it.

To confirm this assumption, we analyzed the same mixture of APNVF and the rosin size with ESCA after heat-treating it at 105°C for 10 min. The ESCA C1s spectra are shown in **Fig. 9**.

As expected, the peak assigned to the carboxyl group of the rosin (at binding energy 289.2 eV) showed up in the spectra. Presumably, this peak appeared because the rosin composition was exposed after the mixture particles were melted by the heat treatment. On the other hand, the ESCA N1s spectra of the same sample (not shown) revealed that there was no new chemical bond formed during the interaction of APNVF and rosin size.

These results suggest that the polymer APNVF could interact with rosin size particles and cover the surfaces of the rosin size particles to physically form a stable structure of particles in the sizing process. These results can also support our previous assumption that the polymer APNVF and the emulsion rosin size interact through the mechanism of hydrogen bonding between the formamido group of the polymer and the carboxyl group of the rosin acids [14].



9. ESCA spectra of the mixture of APNVF and rosin size after heat-treating at 105°C for 10 min.

CONCLUSIONS

Two synthesized cationic polymers, aminated poly-NVF and NVF/MATMAC, have been developed as effective retention aids of rosin sizing under alkaline papermaking conditions. The performance of each polymer depends not only on its chemical structure but also on its molecular weight. The performance was also correlated with pH and was found to depend on the polymer's cationic properties in the alkaline range studied. Partially aminated poly-NVF was more efficient as a co-retention aid than was the copolymer of NVF with MATMAC.

The addition order of the polymer APNVF influenced the sizing performance, supporting the conclusion that the polymer's molecular weight affects its performance. The effect of polymer molecular weight is most likely attributable to the polymer's behavior in penetrating pores. The results of ESCA analysis revealed that the polymer APNVF could interact effectively with the rosin size particles to cover their surfaces. As a result, a stable structure of particles would be formed so that the rosin size microparticles could be retained on the fiber surfaces during the alkaline sizing process. **TJ**

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INSIGHTS FROM THE AUTHORS

In this part of our research, we concentrated on the retention function and the mechanism of a partially aminated poly-N-vinylformamide on alkaline paper sizing with acidic rosin size. The results support our previous hypothesis on the interaction of cationic polymers with rosin size particles. Both the polymer APNVF and a copolymer of N-vinylformamide with MATMAC have two functional groups that we had thought may have some special functions that would make them efficient retention aids for alkaline papermaking.

The most difficult aspect of this research was to figure out the mechanism by which polymer molecules interact with rosin size particles. We tried to solve this problem by using an X-ray photoelectron spectrometry (XPS) technique for the first time.

We discovered that the performance of a polymer as a retention aid on rosin sizing depends not only on its chemical structure but also on its molecular weight. The results from XPS analysis of the mixtures of polymer and rosin size explained the interaction between the polymers and rosin size. The polymers that physically cover the rosin size particles well effectively retain the rosin size and induce good sizing of paper under alkaline conditions.

Vinylformamide-based cationic polymers are effective and available retention aids for alkaline papermaking. Mills can use these polymers to improve wet-end runnability and reduce production cost. Our next step is to investigate their all-around functions and interaction mechanisms, including their effects on drainage, paper strength, and retention of fiber fines and filler.

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