Aminated Poly-*N*-Vinylformamide as a Modern Retention Aid of Alkaline Paper Sizing with Acid Rosin Sizes

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ABSTRACT: Partially aminated poly-*N*-vinylformamides (APNVF) were prepared by the hydrolysis of PNVF and used as the retention aid of rosin size. The dual retention aids system, consisting of this modern polymer and aluminum sulfate (alum) for neutral-alkaline paper sizing using acid rosin sizes, was evaluated by experiment. The results indicated that APNVF was very effective and a small amount of the polymer used together with alum considerably increased the size retention and sizing degree of paper under neutral-alkaline conditions. The cationic charge density of APNVF significantly influenced the sizing efficiency of the rosin sizes. Furthermore, the retention of alkaline filler $CaCO_3$ and paper strength were improved by the polymer addition. It is clear that the polymer can be used as a multifunctional additive for papermaking. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 1805–1810, 2000

Key words: aminated poly-*N*-vinylformamide; retention aid; neutral-alkaline sizing; rosin size; paper strength

INTRODUCTION

For more than 190 years, commercial papermakers have added rosin size and papermaker's alum to an aqueous wood pulp slurry in order to develop the desired degree of water repellency (sizing) in the dried paper product. During most of this period, the commercial rosin size employed has been highly neutralized rosin soap in the form of high solids aqueous paste or liquid.[1] The development of tiny acid rosin particles suspended in water by the emulsification of rosin has provided a more efficient rosin sizing agent. Today, both the rosin soap and the rosin emulsion products are still widely used in the papermaking industry for acidic paper sizing.

However, acidic sizing has several drawbacks, such as yellowing and embrittlement of paper, machine corrosion, and paper strength losses,[2] and the requirements of higher strength paper, the use of calcium carbonate fillers in printing papers, and increased longevity of archival papers prompted the industry to convert to alkaline papermaking.[3] Utilizing neutral-alkaline systems, papermakers have moved away from traditional rosin-alum sizing systems to the use of synthetic sizes such as alkyl ketene dimers (AKD) or alkenyl succinic anhydrides (ASA) and the use of neutral rosin size. However, since the traditional sizing agents, including acid rosin emulsion size and rosin soap size, are easy to prepare and inexpensive, their application to the neutral-alkaline paper sizing is of interest and attractive. Hence, some new retention aids such as cationic starch/aluminum hydroxide microparticulate, polyallylamine/alum, and polyvinylamine/alum systems have already been attempted for this purpose.[4–6] An aminated poly-*N*-vinylformamide (APNVF) prepared by partly hydrolyzing poly-*N*-vinylformamide (PNVF) was also described in a patent[7] as a useful retention aid for the neutral-alkaline sizing using conventional rosin acid size,

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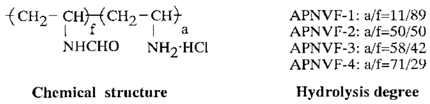

Figure 1 Chemical structure and hydrolysis degree of APNVF used.

although a detailed description was not supplied. This polymer seems to be very interesting as a polymer mordant for sizing because of the coexistence of a primary amino group and a formamide group in the same polymer chain.

In this study, a APNVF-alum dual retention aids system was evaluated and is described in detail in terms of the size content, aluminum adsorption, and sizing degree of the paper under neutral-alkaline conditions.

EXPERIMENTAL

Materials

A commercial hardwood bleached kraft pulp (HBKP) was used for paper sheet making. The pulp was previously beaten to a Canadian Standard Freeness (CSF) of 400 mL with a TAPPI (Technical Association of Pulp and Paper Industry) standard beater. Anionic commercial rosin soap size (SPE, Arakawa Chem. Co. Ltd., Japan) and acid rosin emulsion size (OT500J, Japan PMC Co. Ltd., Japan) were used as sizing agents. The cationic polymer used was APNVF prepared by partly hydrolyzing PNVF (MW 3×10^6, Kurita Water Industries Ltd, Japan) based on a method reported in the literature.[8] Moreover, four APNVFs, with different hydrolysis degrees or amino/formamido (a/f) ratio (shown in Fig. 1), were obtained by changing hydrolysis conditions. The a/f values in the APNVFs were calculated according to their cationic charge densities determined by polyelectrolyte titration[9,10] at pH 2.0. Alum used was an analytical grade (Wako Pure Chemical Ind. Ltd., Japan).

Preparation of Handsheets

To prepare handsheets, 1.2% pulp slurry was primarily adjusted to the assigned pH with 0.1 mol/L NaOH or HCl solution under stirring. Then alum solution followed by rosin size (the mode for rosin soap sizing was size followed by alum) and polymer were added to the pulp slurry. The pulp stock was adjusted again to the desired pH with dilute NaOH or HCl and stirred for 3 min. Handsheets with a basis weight of 60 g/m^2 were made according to TAPPI Test Method T 205om-88.

Wet sheets were pressed at 0.35 MPa for 5 min, dried in oven at 105°C for 10 min, and conditioned at 20°C and 65% relative humidity for more than 24 hours.

Analytical Methods

The charge densities of polymers were determined by polyelectrolyte titration with a F-3010 fluorescence spectrophotometer (Hitachi, Japan) using acriflavine hydrochloride (AF) as a fluorescent indicator.[9,10] Sizing degrees of paper sheets were evaluated by Stockigt method (Japan Industrial Standard P 8122). Determination of rosin size content in paper sheets was carried out with the pyrolysis-GC method in which tetramethylammonium hydroxide (TMAH) was used as the methylation agent of carboxyl groups,[11,12] and aluminum content in handsheets was measured using the oxine method.[13] The retention of $CaCO_3$ was determined by using thermogravimetric analysis (TGA) with a Shimadzu TGA-50 thermogravimetric analyzer and the paper tensile strength was tested with an Autograph AGS-1kNG tester (Shimadzu, Japan).

RESULTS AND DISCUSSION

Characteristics of the Polymer

It is known that the chemical structures and charge densities of cationic polymers have great influence on the sizing efficiency of rosin sizes.[5,6] The cationic polymer APNVF used in this study was a partially animated PNVF by the hydrolysis of PNVF with HCl, and its chemical structure is shown in Figure 1. There are both amino and formamido groups in the polymer APNVF, differing from polyvinylamine (PVAm), polyallylamine (PAAm), and polyethyleneimine, which have been tested as retention aids for neutral-alkaline rosin sizing.

Figure 2 shows the charge density variation of the four APNVFs (shown in Fig. 1) as a function of pH. Apparently, the charge densities of the polymers corresponded well with the hydrolysis degrees or a/f values of the polymers, and the higher hydrolysis degree resulted in a higher charge density over the pH region from 2 to 10. It was expected that the differences in charge density

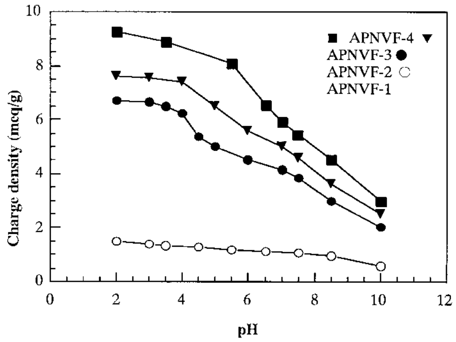

Figure 2 Variation in the cationic charge densities of APNVFs as the function of pH.

would influence the retention behavior of APNVFs on the rosin size. Figure 2 also indicates that the polymer APNVFs were still cationic even at pH up to 10. This feature is of importance to the adsorption of polymer onto pulp fibers and the retention of anionic rosin size particles to fiber surfaces under alkaline conditions.

Sizing Efficiency of the Rosin Sizes with APNVF-Alum Dual Retention Aids

Figure 3 shows the sizing efficiency of the emulsion rosin size OT500J and the rosin soap size SPE with APNVF-alum dual retention aids system under neutral to alkaline conditions. When the cationic polymer APNVF was not added, rosin-alum sizing in the cases of both emulsion rosin size and rosin soap size did not give the required paper sizing degree in the given pH region. However, good sizing effectiveness of the two sizes were achieved when a small amount of APNVF (APNVF-1) was added as co-retention aid at neutral to slightly alkaline pH. The emulsion rosin size especially had moderately high sizing effect even under alkaline conditions where the pH was up to 8. Sawayama et al.[7] also obtained similar results in the patent. Their sizing degrees were 16.4–22.2 s for the rosin soap size and 23.5–29.3 s for the emulsion rosin size when handsheets, with a basis weight of 60.5 g/m^2, were prepared at pH 7.2 under the addition levels of 0.5% rosin size, 0.5% of alum, and 0.05 or 0.1% APNVFs with various degrees (6–95%) of hydrolysis based on pulps, respectively. But there was little effect of the degree of hydrolysis of polymer on sizing efficiency in contrast to our result shown later.

Comparing the sizing degrees of papers, it can be found that the polymer APNVF is more efficient for the emulsion rosin size than for the rosin soap size. This may be related to different interaction features between the rosin sizes and the cationic polymer or between the rosin sizes and aluminum.[14,15] These results suggest that the dual retention aids system, consisting of cationic polymer APNVF and alum, is effective in neutral-alkaline sizing using conventional acid rosin sizes.

In addition, scanning electron microscopy (SEM) showed that the polymer APNVF could effectively prevent the de-emulsification and dissociation of emulsion rosin size particles due to the action of OH^-. As shown in Figure 4a, there was no size particle adsorbed on the pulp fiber surfaces when the paper was sized with the emulsion rosin size and alum without APNVF at pH 7.5 because of the dissolution of rosin size. When 0.1% of APNVF on pulps was used with alum as retention aids in the sizing, however, the rosin size particles adsorbed on the paper surface were clearly observed (as shown in Fig. 4b). This implies that the stability of the size particles, and the retention onto pulps, are responsible for the sizing efficiency of the emulsion rosin size and that one of the important functions of cationic polymer APNVF in the alkaline rosin sizing is to improve the stability of size particles.

Effect of the Polymer Charge Density on the Sizing

Charge density is an important characteristic of cationic polymers, and it affects not only the adsorption of polymers onto pulp fibers but also the retention of rosin size.[14–16] Figure 5 shows the effect of charge density of the polymer on the rosin sizing. According to Figure 2, the charge densities of the four APNVFs at pH 7.5 were 1.1 meq/g for APNVF-1, 3.9 meq/g for APNVF-2, 4.6

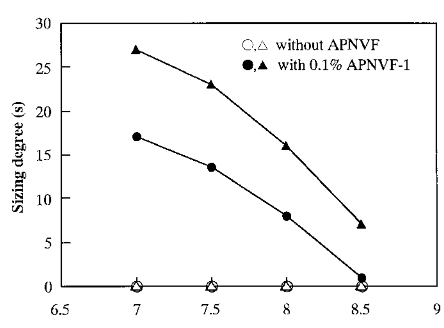

Figure 3 Effect of APNVF-1 on the sizing degrees of paper sized with 0.5% rosin size OT500J (△, ▲) and SPE (○, ●) and 1% alum at different pHs.

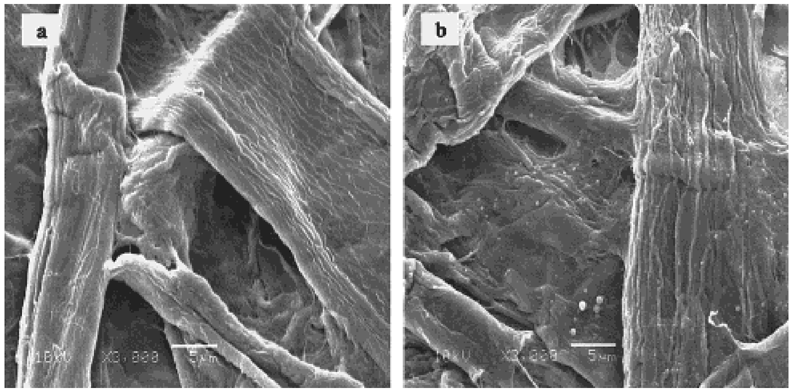

Figure 4 SEM images of the fiber surfaces of paper sized with 1% acid rosin emulsion size and 1% alum without APNVF (a) and with 0.1% APNVF-1 (b) at pH 7.5.

meq/g for APNVF-3, and 5.5 meq/g for APNVF-4, respectively.

As shown in Figure 5, the four APNVFs with same molecular weight but different cationic charge densities induced differences in the sizing of emulsion rosin size with the polymer-alum dual retention aids system. Among the APNVFs, APNVF-1 with the lowest charge density was the most efficient to size retention, effective aluminum adsorption, and consequently the sizing degree. In this respect, Sawayama et al.[7] obtained different results: the effect of APNVFs on sizing degrees were almost the same (23.5–25.1 s) in spite of the great differences (6–95%) in the degree of hydrolysis of polymer.

It was clear, however, that the charge density of the polymer influenced both the size retention and aluminum adsorption in the sizing. APNVF, with lower charge density, was more effective than APNVF with higher charge density for emulsion rosin sizing under neutral-alkaline condition. This phenomenon is most likely correlated to the hydrogen bonding of the polymer molecules with the rosin particles and the coordination bonding of the polymer molecules with aluminum ions. The hydrogen bonding could be formed through the interaction between formamide group in APNVF and the carboxyl group in rosin size.[14,15] The formation of coordination bonding was supported by a significant increase in the cationicity of APNVF by the addition of alum at pH 7.5.[14,15] It may be important that the above phenomena take place cooperatively and contribute to the increase of retention and the correct orientation of rosin sizes.

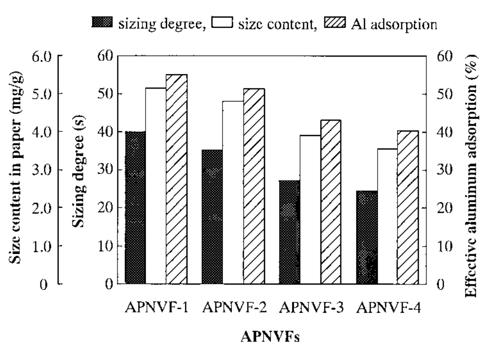

Figure 5 Sizing features of paper sized with emulsion rosin size and APNVF-alum dual retention aids system at pH 7.5. Dosage of size, alum, and APNVF was 1%, 1%, and 0.1%, respectively.

Sizing Behaviors of the New System in Pulp Suspension Containing $CaCO_3$

The use of alkaline filler calcium carbonate is one of the characteristics of alkaline papermaking. Conventional rosin acid sizes, especially rosin soap size, was considered to be ineffective in the sizing of paper using calcium carbonate as filler. It is of interest to know whether the good sizing of rosin acid size with polymer-alum retention system can be achieved in the presence of alkaline filler. Hence, the sizing efficiency of rosin soap with APNVF-alum dual retention aids in the pulp suspension containing calcium carbonate was elucidated in order to evaluate the properties of retention aid APNVF.

Figure 6 shows the sizing degrees of paper as a function of calcium carbonate and the filler retention in this sizing system. According to Figure 6, although it continued to decrease with increasing the amount of $CaCO_3$ in pulp suspension, the sizing degree of paper was still high even at addition levels of $CaCO_3$ over 20%. Obviously, neu-

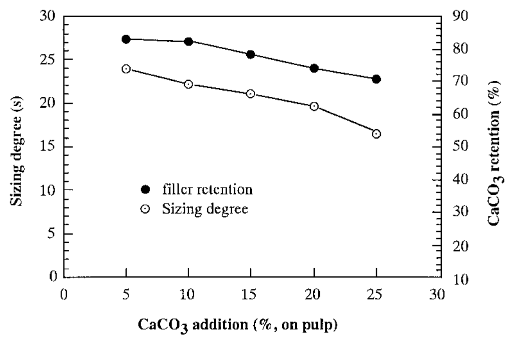

Figure 6 Sizing degree and filler retention of paper sized with 1% rosin soap size, 1% alum, 0.1% APNVF-1, and different amount of $CaCO_3$ at pH 7.5.

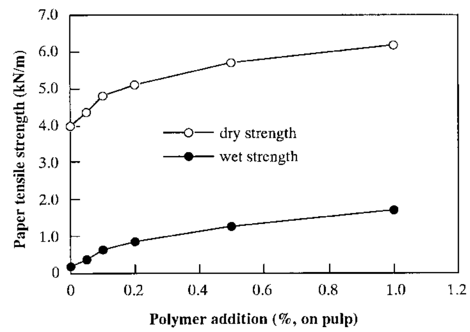

Figure 8 Effect of APNVF-1 addition on the tensile strength of dry paper and wet paper.

tral-alkaline rosin soap sizing with APNVF-alum, a modern dual retention aids system, gave the paper good sizing even in the presence of alkaline filler $CaCO_3$. The results shown in Figure 6 also indicate that the higher retention of filler could be obtained despite its declination after the filler addition over 10%. Gill showed that the degree of agglomeration and retention of calcium carbonate were quite low when polymer was not added.[17] The results of this work disclosed that the alkaline filler $CaCO_3$ was retained well on the paper at a level of around 80%, due to the APNVF addition. Furthermore, SEM observation of paper revealed that the distribution of $CaCO_3$ filler particles on the paper surfaces was dramatically different between the two cases of with and without APNVF as shown in Figure 7. The filler particles were agglomerated and the amount of filler particles retained on the fiber surfaces was clearly increased when 0.1% APNVF was added to the sizing system (Figs. 7a and 7b).

Improvement of Paper Strength by Polymer Addition

It has been known that starch and polyacrylamide can be employed effectively as dry strength additives of paper.[18] It is also very interesting to know whether the polymer APNVF has the function of improving paper strength or not. In order to evaluate the strengthening property of the polymer, paper sheets sized with 1% emulsion rosin size, 1% alum, and different addition levels from 0 to 1.0% of APNVF at pH 7.5 were made, and their dry strength and wet strength were tested respectively. Figure 8 illustrates the effect of polymer on the tensile strength of dry paper and wet paper. It is obvious that both the dry strength and the wet strength of paper sheets were enhanced by the APNVF addition at each level. When the addition level of polymer APNVF was reached at 1% based on dried pulp, the dry strength of paper was improved by around 50% as well as the wet strength being retained at about 25% of the dry strength. The improvement of pa-

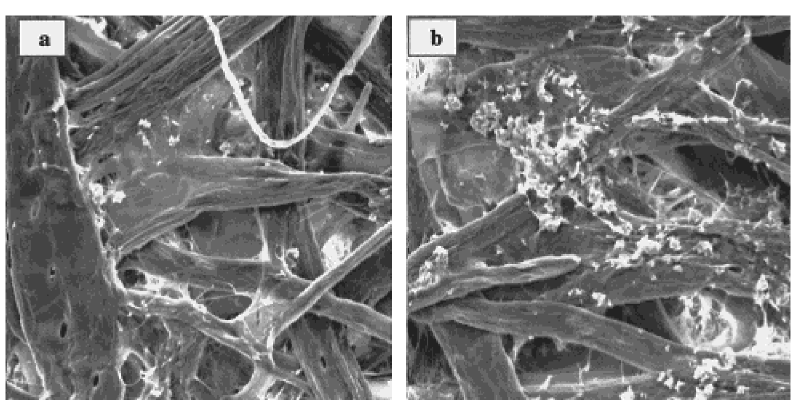

Figure 7 SEM image of paper sized with 1% rosin size, 1% alum, and 15% $CaCO_3$ at pH 7.5, (a) without APNVF and (b) with 0.1% APNVF-1.

per strength is most likely because of the enhanced interfiber bonding mechanism by the strong hydrogen bonding between pulp fibers through polymers. These results suggest that the modern polymer APNVF also had favorable function on the improvement of paper strength, in addition to good retention performance on the rosin size of aluminum and alkaline filler, and would be a multifunctional additive for papermaking.

CONCLUSIONS

APNVF was used as the retention aid of acid rosin sizes, and the dual retention aids system of polymer-alum for neutral-alkaline sizing of acid rosin sizes was evaluated. The results indicated that APNVF was very effective and it would improve the retention of rosin size as well as the adsorption of effective aluminum, consequently enhanced the sizing effectiveness under neutral-alkaline condition, in which acid rosin size-alum sizing is impossible and not practical. The cationic charge density of APNVF apparently influenced the sizing features of paper, and the APNVF with lower charge density was more efficient than the APNVF with higher charge density for the emulsion rosin sizing. For the neutral-alkaline sizing with emulsion rosin size, one of important roles of the polymer was to improve the stability of emulsion rosin size particles at neutral-alkaline pH regions. Furthermore, the APNVF-alum dual retention aids system made it available to size paper effectively with rosin soap size, which has been considered as the most sensitive to calcium carbonate, in the high $CaCO_3$-containing pulp suspension system. On the other hand, the retention of filler $CaCO_3$ was significantly enhanced by the addition of APNVF because of its aggregation function on the calcium carbonate particles, and both the dry tensile strength and wet tensile strength of paper were improved by the polymer.

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