Synthesis of Poly[vinylamine-co-(sodium acrylate)] and its Application as a Paper Strength Additive

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The synthesis of poly[vinylamine-co-(sodium acrylate)] [P(VAm-co-NaAA)] and its application as a paper strength additive have been investigated. P(VAm-co-NaAA) was synthesized by the alkaline hydrolysis of poly[N-vinylformamide-co-(acrylic acid)] (PNVFAA). The influence of polymer concentration, hydrolysis temperature, and NaOH concentrations on the extent of hydrolysis were examined experimentally. The hydrolysis was 100% completed under the following conditions: hydrolysis temperature 80 °C, hydrolysis time 8 h, polymer concentration 2%, and NaOH concentration 0.045 mol/g of PNVFAA. P(VAm-co-NaAA) obtained in this manner increased the tensile strength and folding endurance of paper by 44% and 48%, respectively, and the strength increase was greater than that obtained with the commercially available polyvinylamine.

Keywords: N-vinylformamide; Synthesis; Application; Strength; Poly[vinylamine-co-(sodium acrylate]

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INTRODUCTION

Soluble co-polymers are widely used as papermaking additives and have found application also as stimulus-responsive materials, biomaterials, and chemical modifiers. N-vinylformamide (NVF) is a low toxicity isomer of acrylamide, which can undergo free radical polymerization to produce water-soluble poly(N-vinylformamide) (PNVF) (Badesso *et al.* 1995). This polymer seems to be a convenient precursor of polyvinylamine (PVAm), although alternative synthetic routes for PVAm have been reported in the literature (Reynolds and Kenyon 1947; Hart 1959; Tanaka and Senju 1976). Various co-polymers of NVF have found industrial applications and have attracted much commercial and academic interest. In particular, copolymers of NVF with methyl methacrylate and styrene have a broad range of commercial applications (Pinschmidt *et al.* 1996), which include coatings (Pinschimdt and Chen 1998), water treatment (Burkert *et al.* 1984), and paper manufacture (Moench *et al.* 1993).

As noted in a review article (Wang and Tanaka 2000), aminated PNVF copolymers were used as a retention aid for rosin size; such treatment increased the size retention and sizing degree of paper under neutral-alkaline conditions. This polymer also improved the retention of $CaCO_3$ filler and the paper strength. Copolymers of NVF can play an important role as retention aids along with the conventional polymers such as cationic acrylamide, anionic acrylamide, and polyethylene oxide (Hubbe *et al.* 2009).

PNVFAA, formed by copolymerization of N-vinylamide and acrylic acid in THF solution, may have potential applications in various fields. Its alkaline hydrolysis leads to a polyampholyte P(VAm-co-NaAA) (modified PVAm), as shown in Fig. 1. Modified

PVAm might be used in the preparation of polymeric water-soluble dyes (Dawson *et al.* 1976), polymer surfactants (Qiu *et al.* 1998), mimicking natural enzymes (Martel *et al.* 1994), and is a potential paper strength additive. Commonly used dry-strength additives for paper include water-soluble natural and synthetic polymers, such as starch, guar gum (Dugal and Swanson 1972; Leech 1954), copolymers of acrylamide (Farley 1987; Reynolds and Wasser 1980), and carboxymethylcellulose (Beghello *et al.* 1997; Zhang *et al.* 2002; Hubbe *et al.* 2003a; Watanabe *et al.* 2004). P(VAm-co-NaAA), synthesized under mild reaction conditions and with only few byproducts, could be an economical alternative agent.

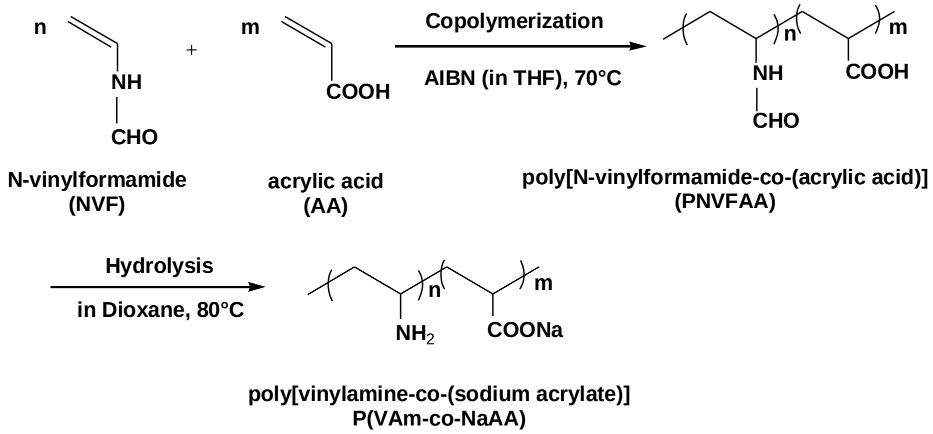


Fig. 1. Synthesis of P(VAm-co-NaAA)

Polyampholytes, containing both positive and negative ionic groups, have also been used as strength additives (Hubbe 2006; Wang *et al.* 2006; Wang *et al.* 2007), and were found to increase the dry strength of paper more than cationic or anionic polymers (Song *et al.* 2006; Hubbe *et al.* 2007), but so far they have not been widely used. Sezaki *et al.* (2006) studied electrokinetic properties and adsorption onto cellulosic fibers of the acrylamide-based polyampholytes. They found that the electrophoretic mobilities of the polyampholytes changed rapidly with pH in the neighborhood of the isoelectric pH values, and polyampholytes with negative net charge also adsorbed onto negatively charged fibers.

In this article, we present a convenient synthesis of P(VAm-co-NaAA) and we discuss the effects of NaOH concentrations, polymer concentration, and hydrolysis temperature on the extent of its hydrolysis. In addition, the strength properties of paper sheets treated with P(VAm-co-NaAA) were measured and the effect of molecular weight of P(VAm-co-NaAA) on paper strength was investigated.

EXPERIMENTAL

Materials

NVF was donated by Tokyo Chemical Industry. Ltd., (Tokyo, Japan) and was distilled under vacuum at 70 °C and stored at -15 °C. Acrylic acid (99%), anhydrous ethanol, hydrochloric acid (HCl), tetrahydrofuran (THF), and dioxane (DME), all from

Tianjin Chemical Reagent Company of China. These, as well as 2,2-azobisisobutyronitrile (AIBN) from Shanghai Petrochemical, were used without any further purification.

Softwood pulp used to create the paper sheets was prepared in the lab. PVAm was synthesized according to a previously published work (Gu *et al.* 2002).

Synthesis of PNVFAA Copolymers

Into a dry 500-mL, three-necked, round-bottom flask, equipped with a magnetic stirring bar and a dropping funnel, 6.25 g (0.0845 mol) of NVF, 2.05g (0.0278 mol) of AA, and 61 mL of anhydrous THF were placed. Then, the initiator azobisisobutyronitrile (AIBN; 20.33 mg, 1.1 mol % relative to the two monomers) dissolved in 20 mL of THF was added to the reaction mixture dropwise over a period of 2 h. The copolymerization was carried out in a water bath for 5 h at 70 °C under a nitrogen atmosphere. After that time, the flask content was poured into 500 mL of a mixture of water and ethanol (30:70), where a precipitate was formed. The byproducts (PNVF, PAA), as well as un-reacted monomers, were removed from the reaction mixture by washing the precipitate at room temperature three times for 30 min with 500 mL of a water/ethyl alcohol mixture using a magnetic stirrer. Then, the precipitate was filtered, dried under reduced pressure at 60 °C for 12 h until reaching a constant weight, and recovered as fine powder. By weighing the product after each wash until constant value, it was found that washing 2 or 3 times is sufficient for the removal of byproducts and un-reacted monomers. The copolymer yield was determined gravimetrically. PNVFAA copolymers with different molecular weights were obtained by varying the molar ratio of initiator AIBN to total monomers. The resulting copolymers were characterized by Fourier transform infrared (IR), proton nuclear magnetic resonance spectroscopy (^{1}H NMR), and (^{13}C NMR) spectra. Equation 1 was used to calculate the extent of copolymer conversion,

$$\text{Copolymer yield} = \frac{a}{b} \tag{1}$$

where *a* is the product weight after the complete removal of byproducts (PNVF, PAA) and un-reacted as described above and *b* is the combined weight of starting monomers.

Hydrolysis of PNVFAA

The hydrolysis of PNVFAA of different molecular weights was carried out as follows. PNVFAA (1 g) and DME (35) mL were added into a 500-mL four-necked bottle equipped with a magnetic stirring bar and a dropping funnel. The mixture was then heated in a water bath and stirred under a N_2 atmosphere for about 30 min until the temperature reached 80 °C. NaOH (18 mL, 2.5N), preheated to the same temperature, was added into the bottle dropwise over a period of 2 h. Then the hydrolyzed copolymer was cooled, acidified with a concentrated HCl solution for 10 min and precipitated by adding 400 mL of ethanol. The resulting copolymer was dried in a vacuum oven at 60 °C for 12 h.

Measurement of Molecular Weight

The P(VAm-co-NaAA) molecular weight was calculated from the solution viscosity according to Mark-Houwink-Sakurada equation (Wagner 1985). The measurement was carried out by a 57 mm inside diameter Ubbelohde viscometer (Hangzhou Hong Wang Technology Co., Ltd. China), using distilled water as the solvent.

Preparation of Paper Sheets

The desired proportion of poly(VAm-co-NaAA) relative to dry fiber was added to the 0.5 % slurry of 23°SR softwood pulp, which was then agitated for 5 min. Handsheets. with a target grammage of 80 g/m^2, were prepared using a handsheet former, pressed at 4 MPa for 1 min and dried for 5 min in a sheet dryer at 105 °C. This procedure was used for P(VAm-co-NaAA) dosages of 0.2%, 0.4 % and 0.6 % and also for control runs with PVAm.

Characterization

The composition of the PNVFAA and P(VAm-co-NaAA) were determined by 500 MHz ^{1}H NMR and ^{13}C NMR (Bruker Advance III 500) spectroscopy. D_2O was used as the internal reference and a solvent. The functional groups of the copolymer side chains were detected qualitatively by FTIR spectroscopy using a Bruker Tensor 27.

Mechanical Testing

The folding endurance and tensile strength of paper sheets were tested according to Chinese standard test methods (GB/T 457-2002, GB/T 453-2002). A vertical tensile tester, model Hangzhou PNSHAR, China TTM-500A, and a paper folding tester, model Changchun small testing machine Co., Ltd. China ZZD-25B, were used. Tests were carried out at 25 °C and 50% relative humidity. Crosshead speeds were 4 mm/min for tensile tests and 3 mm/min for folding tests.

RESULTS AND DISCUSSION

IR Spectra Analysis

Figure 2 gives the FTIR spectra of PNVFAA before and after hydrolysis. In this figure, the broad signal with maximum around 3440 cm^{-1} shows the existence of NH (amide), and peaks around 1650 and 1540 cm^{-1} correspond to the stretching vibration of C=O (amide) and the bending vibration of NH (amide), respectively. After hydrolysis, both of these bands disappeared, as shown in Fig. 2b. The signal around 2930 cm^{-1} detected before the hydrolysis can be ascribed to COOH adsorption. The peaks at about 1630 and 1380 cm^{-1}, shown in Fig. 2(b), are carboxylate absorption bands. Comparison of Fig. 2a and 2b indicates that the PNVFAA was hydrolyzed.

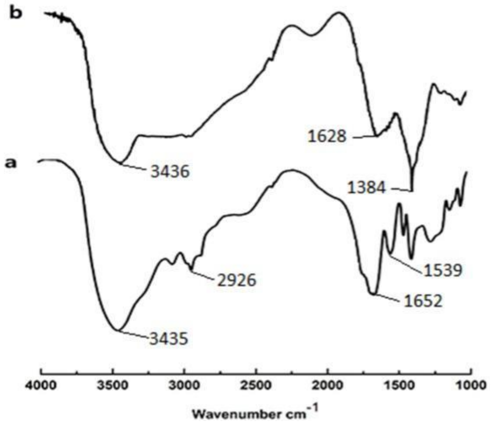
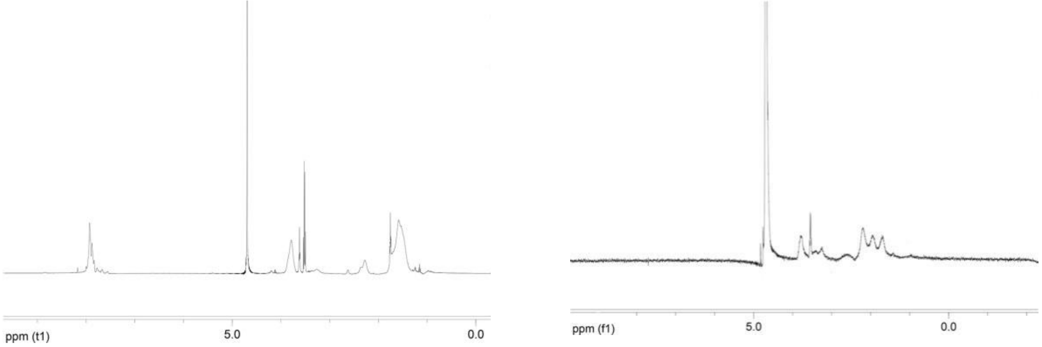


Fig. 2. FTIR spectra of PNVFAA: a: before hydrolysis; b: after hydrolysis

^{1}H NMR and ^{13}C NMR Analysis

Figures 3a and 3b display the ^{1}H NMR spectra of PNVFAA before and after hydrolysis, and Fig. 4 displays its ^{13}C NMR spectrum before hydrolysis. The peaks at (3.4 to 3.8 ppm) and (1 to 1.8 ppm) in Fig. 3a can be assigned to methyne protons and methylene protons, respectively; the peak at 7.9 ppm is indicative of amide protons. After complete hydrolysis, the peak at 7.9 ppm vanished from the spectra, as shown in Fig. 3b. In Fig. 4 the peaks at 163 ppm and 179 ppm can be ascribed to the carbon signals of amide and carboxyl groups, respectively. These spectra confirm that the copolymer of PNVFAA had been produced.



a

b

Fig. 3. ^{1}H NMR spectra of PNVFAA: a: before hydrolysis; b: after hydrolysis

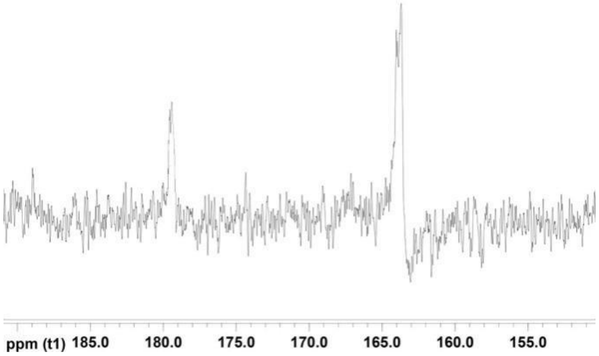


Fig. 4. ^{13}C NMR spectra of PNVFAA

Determination of the Extent of PNVFAA Hydrolysis

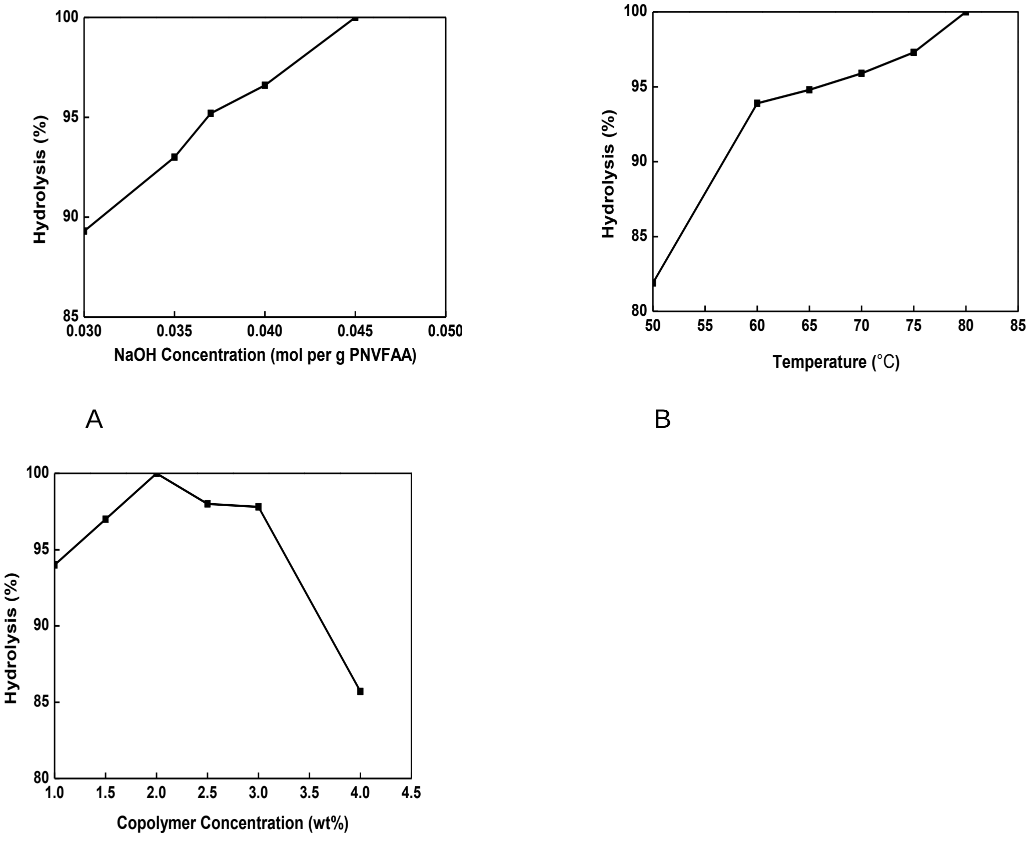
During hydrolysis, NaOH first neutralized the carboxyl groups of PNVFAA and then caused hydrolysis of amide groups. The extent of the PNVFAA hydrolysis was determined by a comparison of ^{1}H NMR signal intensities of the amide group protons (7.9 to 8.1 ppm) and the signal intensities of the backbone methyne protons and methylene protons at 3.4 to 3.8 ppm and 1 to 1.8 ppm, respectively. The area of the amide group peak diminished with increasing degree of hydrolysis.

Influence of NaOH Concentration on the Extent of Hydrolysis

The influence of NaOH addition on the extent of hydrolysis was studied using NaOH concentrations of 0.030, 0.035, 0.037, 0.040, and 0.045 mol per g of PNVFAA. The copolymer concentration, reaction time, and reaction temperature were kept at constant values of 2 %, 8 h, and 80 °C, respectively. The results are shown in Fig. 5A. The NaOH addition had a great influence on the extent of PNVFAA hydrolysis. The extent of PNVFAA hydrolysis increased with increasing amounts of NaOH. When the NaOH concentration was 0.045 mol, the hydrolysis was 100% completed. On the other hand, at NaOH concentration of 0.030 mol, only 89% of the polymer was hydrolyzed.

Influence of Temperature on the Extent of Hydrolysis

The hydrolysis of PNVFAA was carried out at 50, 60, 65, 70, 75, and 80 °C. The copolymer concentration, reaction time, and NaOH concentration were kept at constant values of 2%, 8 h, and 0.045 mol per g of PNVFAA, respectively. The results are shown in Fig. 5B. When the temperature was low, the hydrolysis reaction was slow and the extent of hydrolysis was low. However, as temperature increased, the hydrolysis degree increased from 81.9% to 100%.



A

B

C

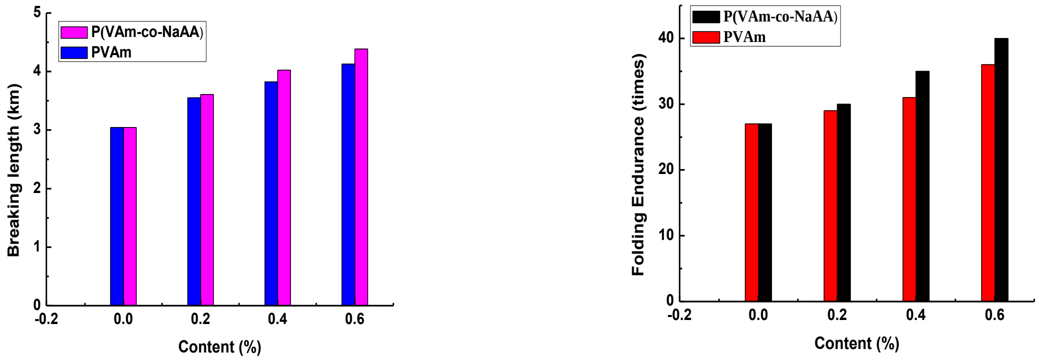
Fig. 5. Hydrolysis of PNVFAA varying (A) NaOH concentration, (B) temperature, and (C) copolymer concentration

Influence of Copolymer Concentration on the Extent of Hydrolysis

The influence of copolymer concentration on the extent of hydrolysis was studied for copolymer concentrations of 1.0, 1.5, 2.0, 2.5, 3.0, and 4.0%. The temperature, reaction time, and NaOH concentration were kept at constant values of 80 °C, 8 h, and 0.045 mol per g of PNVFAA, respectively. The results in Fig. 5C show that the extent of hydrolysis initially increased with increasing copolymer concentration and that hydrolysis was 100% complete when the copolymer concentration was 2%. However, when the copolymer concentration increased beyond 2%, the hydrolysis yield declined; at a concentration of 4%, the yield was only 85%. Thus, the intermediate copolymer concentrations were found to be the most beneficial for the hydrolysis of PNVFAA.

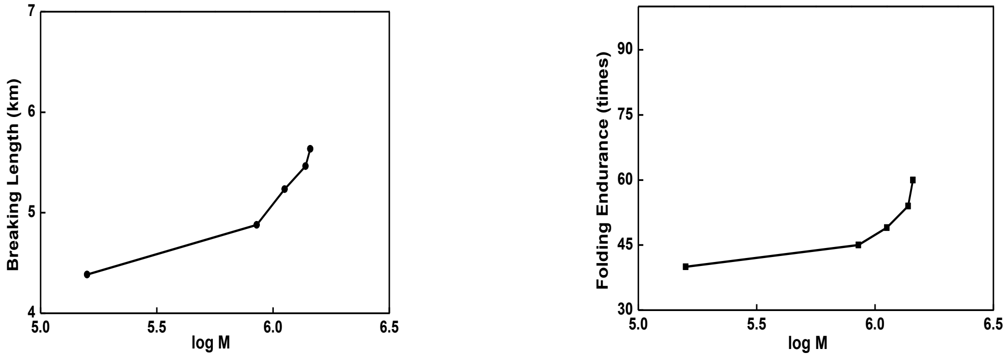
Tensile Strength and Folding Endurance

Figures 6a and 6b demonstrate that the tensile strength and folding endurance of paper sheets improved with increasing content of P(VAm-co-NaAA). To compare the strengthening effect of a polyampholyte with the commonly used cationic polymer we tested also handsheet prepared with the addition of PVAm. From Figs. 6a and 6b it is evident that P(VAm-co-NaAA) increased strength properties of paper more than recently-introduced, strongly-cationic PVAm. This result might indicate that the combination of cationic amino group and anionic carboxylate groups of polyampholyte P(VAm-co-NaAA) increases fibre bonding more than the just the positive charges of cationic PVAm.



a b

Fig. 6. The effect of P(VAm-co-NaAA) content on the (a) tensile strength and (b) folding endurance of handsheets



a b

Fig. 7. The effect of the molecular weight of P(VAm-co-NaAA) on the (a) tensile strength and (b) folding endurance of handsheets

Influence of the Molecular Weight of P(VAm-co-NaAA) on Paper Strength

The tensile strength and folding endurance of paper sheets increased with increasing the molecular weight of P(VAm-co-NaAA) as shown in Figs. 7c and 7d. Paper impregnated with P(VAm-co-NaAA) having the molecular weight of 1.43 million daltons had 1.5 times greater folding endurance and almost 1.3 times greater tensile strength when compared to paper treated with similar additive but having the lower molecular weight of only 0.156 million dalton. The correlation of the polymer strengthening effect and its molecular weight has been observed also by other authors (Pelton *et al.* 2003).

CONCLUSIONS

1. A novel potential paper strength additive, P(VAm-co-NaAA), was synthesized by alkaline hydrolysis of PNVFAA. The extent of hydrolysis strongly depended on polymer concentration, hydrolysis temperature, and NaOH concentration. The hydrolysis reached 100% under the following conditions: temperature 80 °C, time 8 h, polymer concentration 2%, and NaOH concentration 0.045 mol per g of PNVFAA.
2. The P(VAm-co-NaAA) increased the tensile strength and folding endurance of handsheets, and in these respects, it performed better than PVAm. The ability of P(VAm-co-NaAA) to strengthen paper increased with increasing molecular weight. paper impregnated with P(VAm-co-NaAA) having the molecular weight of 1.43 million daltons had 1.5 times greater folding endurance and 1.3 times greater tensile strength compared to paper treated with a similar polymer having M.W. of 156000 Dalton.

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