

Influence of Retention System and Curing on Paper Wet Strength Improvement by a Copolymer Containing Glycidyl Groups

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ABSTRACT: The copolymer (PGS) synthesized by polymerization of glycidyl methacrylate with styrene had a significant effect on paper wet strength. Factors such as retention aids, curing temperature, and curing time were investigated. The results showed that among four kinds of partially aminated poly *N*-vinylformamide (APNVF), APNVF-4 that had the highest charge density was the most effective for strengthening paper. The effectiveness of the retention systems increased with their wet functionality in the order APNVF-4 > C-PAM \approx PAAm > PEI > PDADMAC. The curing temperature and curing time had little influence on paper dry strength, but they influenced paper wet strength greatly. The FTIR studies on model reactions showed that glycidyl groups could react with amino groups and carboxyl groups under common curing conditions. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2791–2797, 2001

Key words: papermaking; paper wet strength; glycidyl groups; crosslinking; FTIR spectroscopy

INTRODUCTION

The strength of paper and board is reduced to less than 10% when it becomes wet, but many kinds of papers such as tissue, paper towel, sanitary paper, filter paper, photographic paper, sack paper, and packaging paper require the certain degree of wet strength. These days urea formaldehyde (UF), melamine formaldehyde (MF) and polyaminoamido-epichlorohydrin (PAE) resins are commonly used. Currently, however, these chemicals have come under scrutiny as generating suspected carcinogens and toxicants.^{1–5} Thus, the development of new wet strength agents and methodologies has been earnestly required.

In our previous work,⁶ we discussed the copolymer (PGS) of glycidyl methacrylate with styrene and the paper wet strength improvement. The polymer containing glycidyl groups can react with materials containing active hydrogen, such as amino, hydroxyl, and carboxyl groups. A significant effect on paper strength was observed. The polyallylamine hydrochloride (PAAm) was used as a retention aid because of the possibility of achieving crosslinking between glycidyl groups and amino groups. In the present study, we prepared two kinds of pulps—hardwood bleached kraft pulp (HBKP) and softwood unbleached kraft pulp (SUKP)—and compared the effects of several kinds of cationic retention aids: partially aminated poly-*N*-vinylformamide (APNVF), PAAm, polyethyleneimine (PEI), cationic polyacrylamide (C-PAM), and polydiallyldimethylammonium chloride (PDADMAC).

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All commonly used wet strength resins must undergo a curing step before they impart wet strength to paper. It is not surprising that a system may have high retention but poor wet strength performance. Most of the present wet strength resins are thermosetting. In the case of PGS, the reaction of glycidyl group with amino group is a low-temperature setting. However, the reaction of a glycidyl group with a carboxyl group of cellulose needs a relatively higher temperature.^{7,8} This study discussed the influence of curing temperature and curing time on paper wet strength enhancement using PGS.

The mechanism of the reactions involved in curing is an important issue for paper wet strength resins. Many studies of the reaction mechanisms of various wet strength resins have been reported. FTIR and proton, ¹³C- and ¹⁵N-nuclear magnetic resonance (NMR) spectroscopy can be used to study wet strength resins.^{9–11} Mechanistic studies are more difficult at low levels of addition. It is common practice to optimize the conditions of a proposed reaction step on a model compound bearing the same functional groups.¹² This study simulated the reaction of a glycidyl group with an amino group and the reaction of a glycidyl group with a carboxyl group at the curing temperature. The results paralleled the wet strength improvement effect of PGS reported previously.

EXPERIMENTAL

Materials

HBKP at 320 mL CSF (Canadian Standard Freeness) and SUKP at 400 mL CSF were prepared. All the pulps were completely dispersed in water by a TAPPI (Technical Association of Pulp and Paper Industry) standard disintegrator. PGS was prepared by emulsion polymerization of glycidyl methacrylate with styrene at a molar ratio of 1 : 1.⁶ PAAm with DP 70,000 was a commercial product (from Aldrich). Methacrylic acid (MAA) and glycidyl methacrylate (GMA) were of reagent grade, and were used without further purification.

Partially aminated poly-*N*-vinylformamide (APNVF) was prepared by hydrolyzing poly(*N*-vinylformamide). The charge densities of four APNVFs were determined by polyelectrolyte titration using a F-3010 fluorescence spectrophotometer (Hitachi, Japan) and acriflavine hydrochloride

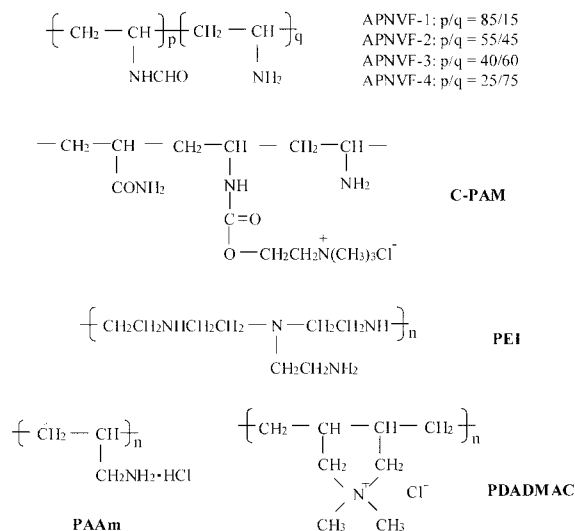


Figure 1 Chemical structures of retention aids used in this study.

(AF) as a fluorescent indicator.^{13,14} Solutions of PDADMAC and PEI were made using commercial products. C-PAM that contains both primary and quaternary amines was prepared according to the Hofmann reaction by adding choline chloride to a solution of PAM in water.¹⁵

The chemical structures of retention aids used are given in Figure 1.

Preparation and Determination of Paper Sheets

To disintegrated pulps at a consistency of 1.2%, 0.2% retention aids on pulp were added under stirring. After 1 min, PGS solution was added at a level of 2% on the paper and stirred for 3 min. Handsheets (60 g/m²) were made according to TAPPI standard T205 om-88. The sheets were cured by heating in an oven at 105°C for 20 min unless otherwise noted in the text, and were then conditioned at 25°C and 65% RH for more than 24 h. Wet strength was determined after soaking the sheets in deionized water for 1 h and then removing surface water with filter paper as quickly as possible. The tensile strength was measured according to TAPPI standard T494 om-88. The mean of three replicates, which agreed to less than 5% from that, is given in figures.

FTIR Spectroscopy

Model reactions of GMA with PAAm and of GMA with MAA were studied by FTIR spectroscopy. A mixture of GMA and PAAm was heated at 105°C for 10 min and a mixture of GMA with MAA was

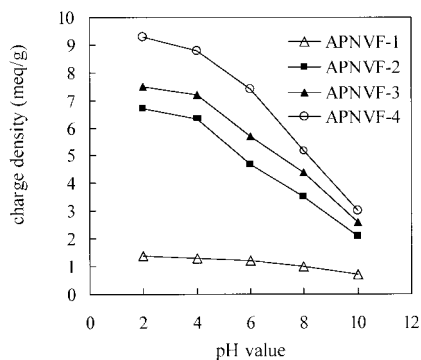


Figure 2 Charge densities of APNVFs water solutions at different pH values.

heated at 105°C for 20 or 40 min for FTIR determinations. Potassium bromide powder was used as a reference material to produce a background diffuse reflectance spectrum. A Perkin-Elmer System 2000 FTIR spectrometer was used in the transmission intensity mode. Scannings were repeated 100 times for each sample at a resolution of 4 cm⁻¹.

RESULTS AND DISCUSSION

Paper Strength Improvement with PGS Using Different Retention Systems

The cationic polymer APNVFs used in this study were partially aminated poly-*N*-vinylformamides obtained by the hydrolysis of poly-*N*-vinylformamide. APNVF-1, APNVF-2, and APNVF-3 were prepared by acid hydrolysis, and APNVF-4 was prepared by alkaline hydrolysis. The general chemical structure of APNVF is given in Figure 1.

APNVF molecules contain both amino groups and formamido groups. The four kinds of APNVFs used in the study have different degrees of substitution of formamido groups by amino groups. The charge densities of the four APNVFs were determined by polyelectrolyte titration using potassium polyvinylsulfonate (PVSK) as an anionic polyelectrolyte titrant. The results are shown in Figure 2. The charge densities of APNVFs decreased with increasing pH. More than half the protonated amino groups remained at pH = 7.5, at which the present papermaking was performed. It confirmed that APNVFs could be used as retention aids for PGS under near neutral conditions.

Figure 3 shows the dry strength of HBKP sheets and SUKP sheets using different APNVFs

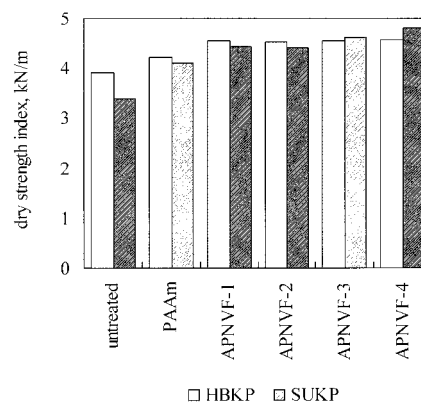


Figure 3 Dry strength index of sheets added with 0.2% of different APNVFs and 2% of PGS, curing temperature: 105°C, curing time: 20 min.

as retention aids for the PGS. The level of APNVF was 0.2% and PGS was 2% based on the bone-dry pulp. The figure shows that the strength improvement with all APNVFs was better than with PAAm as a retention aid for PGS. There was no great difference between the four APNVFs.

In the case of wet strength improvement by PGS, there were large differences between the four APNVFs. APNVF-4 with NHCHO : NH₂ = 1 : 3 showed a higher wet efficiency than the others. Figure 4 shows the wet strength index achieved with different APNVFs. The APNVFs showed a better wet strengthening effect than PAAm, except for APNVF-1, which had the low content of an amino group. This is possibly because the molecular weight of APNVFs was much larger than that of PAAm (Table I), that they had advantages in crosslinking. Also, the reaction of formamido

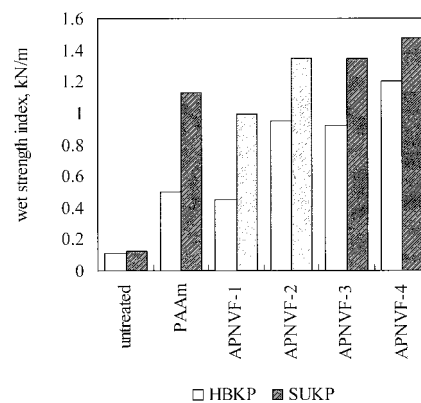


Figure 4 Wet strength index of sheets added with 0.2% of different APNVFs and 2% of PGS, curing temperature: 105°C, curing time: 20 min.

Table I Molecular Weights and Charge Densities of Different Retention Aids

Polymer	MW	Charge Density (mEq/g)
PAAm	7.0×10^4	7.6
APNVF-4	3.0×10^6	5.8
PEI	5.0×10^5	9.6
C-PAM	5.5×10^5	0.6
PDADMAC	2.5×10^5	4.8

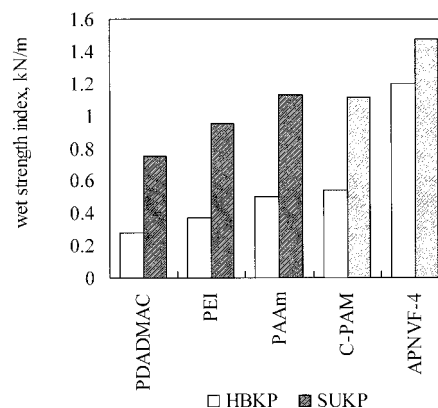
groups with cellulose should occur during the curing. The wet effectiveness of APNVF-2 and APNVF-3 was similar for both HBKP and SUKP sheets. Both the wet and dry strengths of SUKP sheets improved more than those of HBKP sheets using the PGS treatment.

Results showed that the retention system influenced the wet strength more than the dry strength when PGS was used. The effectiveness of the APNVFs increases with their wet functionality in the order APNVF-4 > APNVF-3 \approx APNVF-2 > APNVF-1. Although the APNVFs have the same MW = 3.0×10^6 , the charge densities are different, so the retention and crosslinking characteristics with PGS are different.

Because APNVF-4 is the best one of the four APNVFs for PGS addition as a retention aid, it was selected and compared with other cationic retention aids: PDADMAC, PEI, PAAm, and C-PAM. The chemical structures of the cationic polymers are given in Figure 1. The molecular weights (MW) and charge densities at pH 7.5 of the polymers are shown in Table I.

The application of PGS using different retention aids for HBKP sheets and SUKP sheets were studied. The result indicated that the effectiveness of the different retention aids on the dry strength using PGS was almost the same. The sheet with C-PAM showed a slightly higher dry strength than the others. The effects of different retention aids on SUKP sheets were similar to those on HBKP sheets.

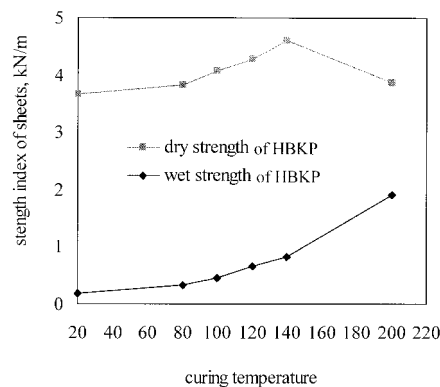
The changes in wet strength are shown in Figure 5. Compared with the effects on dry strength, the effects of different retention systems on paper wet strength had larger differential using PGS as wet strength agent. APNVF-4 had the best effect on wet strength improvement together with PGS. C-PAM had almost the same effect as PAAm, and PDADMAC showed the lowest effect on paper wet strength improvement. The effectiveness of the retention aids increases with their wet function-

**Figure 5** Wet strength index of sheets added with 0.2% of different retention agents and 2% of PGS, curing temperature: 105°C, curing time: 20 min.

ality in the order APNVF-4 > C-PAM \approx PAAm > PEI > PDADMAC, both for HBKP and SUKP sheets.

Influence of Curing Temperature and Curing Time

PGS is a thermosetting resin, and the effects of curing conditions on its efficiency are, therefore, important in its applications. This study was undertaken to investigate the effects of curing temperature and curing time on the wet strengthening effectiveness of PGS. Figure 6 shows the dry and wet strengths of HBKP sheets with added PAAm and PGS for different curing temperatures. The curing time was 20 min for each sample. The dry strength of the sheets increased with increasing curing temperature up to 140°C, and decreased when the curing temperature was

**Figure 6** Influence of curing temperature on paper dry and wet strengths using PGS addition, curing time: 20 min.

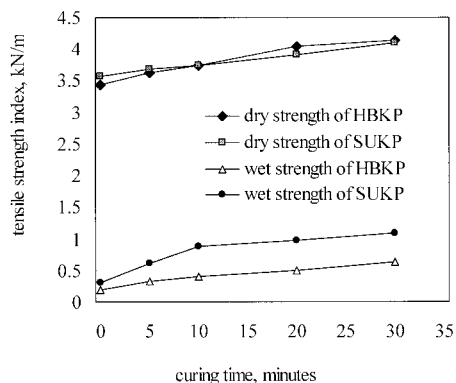


Figure 7 Relationship between curing time and paper dry and wet strengths, PAAm: 0.2%, PGS: 2%, curing temperature: 105°C.

200°C. High temperature would make the fibers brittle and, therefore, reduce the strength of sheets. On the other hand, the wet strength continued to increase even at a curing temperature of 200°C. The influence of curing temperature was greater on paper wet strength than on paper dry strength.

The influence of curing time was also investigated. Figure 7 shows the relationship between curing time and the dry and wet strengths of paper. The curing temperature was 105°C. PAAm 0.2% was added as a retention aid, and PGS 2% was used as a wet strength agent. The paper dry strength increased with increasing curing time for both HBKP and SUKP sheets. However, the increment was not significant. The dry strengths of the HBKP and SUKP sheets tended to be identical.

SUKP sheets showed higher wet strength improvement than HBKP sheets with increasing curing time. There was an obvious increase in paper wet strength during the first 10 min curing at 105°C. After that, the wet strength of both HBKP and SUKP sheets with PGS addition leveled off. Most of the functional groups of the polymers should have reacted during the initial stage. Prolonging the curing time gave no further improvement of wet strength at the given curing temperature.

FTIR Spectroscopic Study of the Wet Strengthening Mechanism of PGS

PGS consists of carbon, hydrogen, and oxygen elements that are also present in cellulose. It is very difficult to distinguish the similar groups in

spectroscopic studies such as the FTIR technique. The absorbance of ester groups in PGS is close to that of carboxyl groups in cellulose. The reaction products of glycidyl groups with amino groups or carboxyl groups are mainly hydroxyl groups, ester groups, and ether, and these are difficult to distinguish from the groups originally existing in the pulp. In addition, the added amount of the polymers was very small (less than 5%), and they were, therefore, difficult to detect in spectroscopic studies. In this research, we applied FTIR spectroscopy to study the model reactions of glycidyl methacrylate (GMA) with PAAm, and the reaction of GMA with methacrylic acid (MAA). The characteristic absorbance of the epoxy group appeared at 913 cm^{-1} . The band intensity was used to evaluate the extent of reaction of glycidyl groups during the curing process.

At first, the mixture of GMA and PAAm was prepared in the molar ratio of 1 : 1. A part of the mixture was used for FTIR recording and a part of it was first heated at 105°C for 10 min. The spectra are given in Figure 8. In the spectrum of the mixture before heating, there is an obvious epoxy band at 913 cm^{-1} . After heating at 105°C for 10 min, the peak at 913 cm^{-1} disappeared. This confirms that the reaction of the glycidyl group with the amino group could easily occur under the given curing conditions. Therefore, the polymers with amino groups acted not only as retention aid but also participated in the reactions and increased the paper wet strength

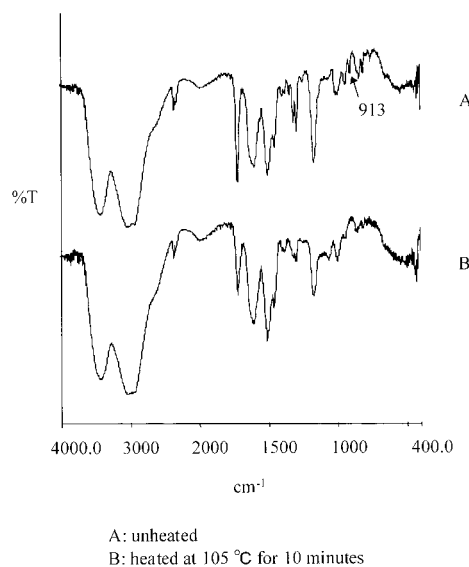


Figure 8 FTIR spectra of mixture of GMA and PAAm at the molar ratio of 1 : 1.

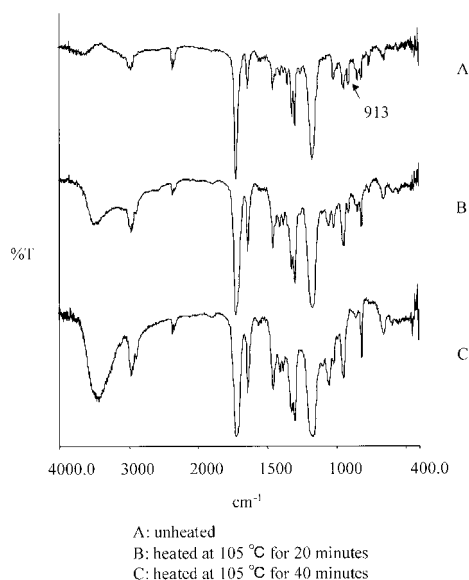


Figure 9 FTIR spectra of mixture of GMA and MAA at the molar ratio of 1 : 1.

greatly. The resultant secondary amine could also react with the glycidyl group but at a lower speed than primary amine.¹⁶

The reaction of glycidyl groups with undissociated carboxyl groups was considered to take place very slowly, but the COO^- can react with glycidyl groups more easily.⁸ In fact, the paper prepared at pH 7.5 in the presence of PGS had a high wet strength, as described in the previous article.⁶ In this study, the mixture of GMA and MAA was prepared in a molar ratio of 1 : 1 and the FTIR spectrum of the mixture was determined. The mixture of GMA and MAA was then heated at 105°C. The extent of reaction was traced by the FTIR determination. Figure 9 shows the decrease in the characteristic epoxy band at 913 cm^{-1} during the heating. In the case of the unheated mixture, there is an obvious band at 913 cm^{-1} . After the mixture had been heated for 20 min, the peak at 913 cm^{-1} decreased, and the peak at 3500 cm^{-1} showed a stronger absorbance. This is due to a stretching vibration of hydroxyl groups, which resulted from the reaction of glycidyl groups and carboxyl groups. Because the mixture still contained epoxy groups after it had been heated for 20 min, it was suggested that the reaction did not finish under these curing conditions. The peak at 913 cm^{-1} was found to have disappeared after heating for 40 min. This confirmed that carboxyl groups could react with glycidyl groups at 105°C after a prolonged curing process. The band at 3500 cm^{-1} for hydroxyl groups increased further in intensity after the heating.

The results of FTIR spectroscopic studies indicate that the copolymer containing glycidyl groups can react with amino groups of other polymers to form homo-crosslinking, and with carboxyl groups of cellulose to form cocrosslinking under common curing conditions and thus improve paper wet strength.

CONCLUSIONS

Among the four APNVFs that contain both amino groups and formamido groups, APNVF-4, with a higher charge density, exhibited the greatest paper wet strength improvement when used as retention aid for PGS. The wet strength effectiveness of APNVFs together with PGS was more significant for SUKP than for HBKP sheets. In the case of paper wet strength, the different retention aids exhibited different efficiencies. The effectiveness of the retention aids increases with their wet functionality in the order APNVF-4 > C-PAM \approx PAAm > PEI > PDADMAC.

The curing temperature had a significant influence on paper wet strength improvement. The paper wet strength increased at a higher rate in the initial stage of curing for both HBKP and SUKP sheets.

The model reactions of glycidyl groups with amino groups and carboxyl groups were studied by FTIR spectroscopy. The result showed that the reaction of glycidyl groups with amino groups was completely finished after heating at 105°C for 10 min. The reaction of glycidyl with carboxyl group was relatively slow. Glycidyl groups still remained after 20 min; but they disappeared after heating for 40 min. Because COO^- was shown to react with glycidyl group more easily than COOH , the actual reaction in papermaking should be faster at pH 7.5.

Dr. Anthony Bristow generously made a linguistic revision of the manuscript.

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