

Copolymerization of Glycidyl Methacrylate with Styrene and Applications of the Copolymer as Paper-Strength Additive

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ABSTRACT: A copolymer of glycidyl methacrylate and styrene (PGS) was synthesized by emulsion polymerization. The effect of the polymer on paper dry- and wet-strength improvement was investigated. The polymer contains phenyl groups that provide hydrophobic character to fibers so as to improve paper wet performance, and glycidyl groups that react with nucleophilic groups in fibers and other polymers to increase paper strength. Results showed that other polymers, such as polyallylamine, polyacrylic acid, and modified polyacrylamide, could be used together with PGS for paper-strength improvement. Furthermore, three kinds of partially carboxymethylated pulps (CMP) were prepared and used for PGS treatment. Compared with original pulp sheet, the sheets containing CMPs were strengthened greatly both in dry and in wet strength after PGS treatment. It was confirmed that higher CMP content got higher strength improvement at the same addition level of PGS. The results showed that carboxyl groups in pulp participate in the reaction with PGS and the cocrosslinkings between fibers and polymers were formed for improving paper strength. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 334–339, 2001

Key words: glycidyl methacrylate; styrene; copolymer; carboxymethylation; paper; wet-strength agent

INTRODUCTION

It is commonly known that paper loses most of its strength when it contacts with water. To improve paper wet strength, many kinds of polymers have been applied as paper wet-strength additives.¹ Most common ones are urea–formaldehyde (UF), melamine formaldehyde (MF), and polyaminoamide–epichlorohydrin (PAE) resins that can make self-crosslinking.^{2,3} UF and MF resins require acid paper making condition that would cause problems such as equipment corrosion and paper strength diminution. Also, free formaldehyde has

an environmental impact. PAE resin increases the level of absorbable organic halogen (AOX) in mill effluent so that it requires to be reformed. Although polycarboxylic acid was found to make crosslinking between fibers by esterification and then improve paper wet strength,^{4–7} very high temperature (more than 150°C) is required to achieve effective esterification of cellulose.⁵ Polymers containing isocyanate groups were synthesized as paper wet-strength additives.⁸ Because the isocyanate group is highly reactive, it needs further study to put it into actual production.

Glycidyl groups can react with materials containing active hydrogen, such as an amino group, a hydroxyl group, and a carboxyl group⁹ (Fig. 1). It shows promise that the polymer with the glycidyl groups forms linkages not only by reacting

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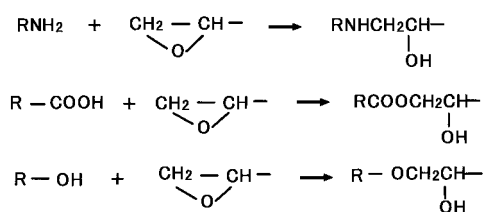


Figure 1 Reactions of epoxy groups with amino, carboxyl, and hydroxyl groups.

with other polymers containing amino or carboxyl groups, but also by reacting with carboxyl groups of fibers. The later will achieve greater paper wet-strength improvement.

In this research, glycidyl methacrylate and styrene were selected as comonomers. When the reaction was performed under room temperature in a redox initiator system, more than 95% of the epoxy groups remained in the resulted latex.¹⁰ The copolymer PGS was added in paper together with polyallylamine (PAAm), which also acts as a retention aid. It was found that PGS had a significant effect on paper-strength improvement under neutral sheet-making conditions. To improve the paper strength furthermore, polyacrylic acid (PAA) and modified polyacrylamide (PAM) that contained amino and carboxyl groups were used instead of PAAm. In addition, carboxymethylated pulps (CMP) with different carboxyl contents were prepared and used to make abundant crosslinkings between fibers and PGS.

EXPERIMENTS

Copolymerization of Glycidyl Methacrylate (GMA) and Styrene

PGS was synthesized by emulsion polymerization. The flask containing 100 g water, 2.5 mL styrene, 3 mL GMA, and 0.33 g sodium dodecyl sulfate as the emulsifier, was cleared of oxygen by nitrogen gas. Sodium persulfate 0.27 g, sodium

hydrogen sulfite 0.12 g, and iron sulfate 0.0001 g and EDTA 0.0001 g were added in the flask as a redox initiator. The reaction was performed at 25°C for 15 h under stirring. A part of the emulsion was lyophilized to powder for FTIR determination.

Modification of Polyacrylamide

First, PAM (MW: 7.0×10^5) in 10% aqueous solution was hydrolyzed with sodium hydroxide (10:1.7 w/w). And then, the resulted solution was allowed to react with sodium hypochlorite (NaOCl/PAM = 0.98 mol/mol, NaOH = 6.0 M) to produce the amino groups. The amount of amino and carboxyl contents of the polymer was determined by colloid titration using a fluorescent indicator.¹¹

Carboxymethylation of Pulp

Bleached hardwood kraft pulps with CSF 400 mL were weighted to a flask. NaOH and water were added and stirred for 1 h at room temperature. Then monochloroacetic acid (MCAA) was added during stirring. The pulps made from different conditions (see Table I) were washed by deionized water until neutral.

Analysis of carboxyl content:^{12,13} pulps were first treated with 0.1 N HCl, and then washed until neutral. Acid-treated pulp 0.5 g was placed in a flask, and a mixture of 0.02 M NaOH 25 mL and 50 g/L NaCl 25 mL was poured into it under nitrogen atmosphere. After 48 h, the pulp was filtered and washed by 50 mL deionized water, and the whole filtrate was collected. Fifty milliliters of the filtrate was taken out and titrated with 0.01 M HCl. The sodium consumption was calculated by comparing it with a blank test. The degree of substitution was expressed as mmol/g pulp.

Sheet Strength Determination

Pulps were completely dispersed in water by a standard disintegrator. A retention aid was then

Table I Reaction Conditions of CMP Preparation

	NaOH : pulp w/w	MCAA : Pulp w/w	Liquor Ratio	Temp. °C	Reaction Time h	COOH Content mmol/g Pulp
Original pulp						0.10
CMP3	1 : 2.5	1 : 1	1 : 25	22	20	0.19
CMP5	1 : 1.25	6 : 5	1 : 32	25	16	0.17
CMP6	1 : 1.25	6 : 5	1 : 32	25	26	0.22

added under stirring. After 1 min, a certain amount of PGS emulsion was added with stirring for 3 min. Hand sheets (60 g/m^2) were made according to TAPPI standard T205 om-88. The sheets were cured by heating in an oven at 105°C for 20 min and conditioned at 25°C and 65% RH for more than 24 h. Sheet wet strength was determined after soaking the sheets in deionized water for 1 h, and then removal of surface water with filter papers as quickly as possible. The tensile strength was measured according to TAPPI standard T494 om-88.

The sizing degree of sheet was determined by a stöckigt test (Japanese Industrial Standard JIS P8122). A paper sample was floated on the surface of 2% ammonium thiocyanate solution in the Petri dish, and a drop of 1% ferric chloride solution was dripped on the sheet at the same time. The penetration time was determined until red ferrithiocyanate spots appeared.

RESULTS AND DISCUSSION

The copolymer synthesized from glycidyl methacrylate and styrene (PGS) contains glycidyl groups and phenyl groups. PGS can give a hydrophobic nature to fibers and react at the same time with materials containing amino and carboxyl groups to form crosslinkings between fibers. The FTIR spectra of GMA and PGS are given in Figure 2, which shows that the double bond peak at 1640 cm^{-1} disappeared and glycidyl band at 913 cm^{-1} remained after polymerization. The glycidyl con-

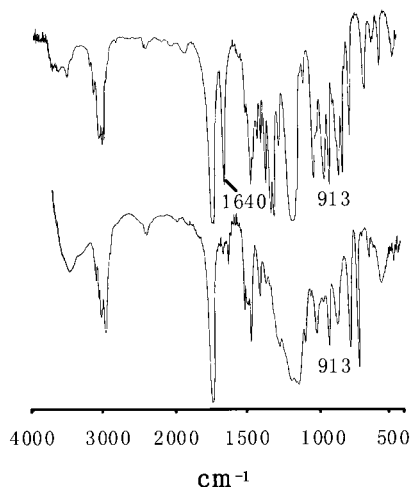


Figure 2 FTIR spectra of GMA (up) and the copolymer PGS (down).

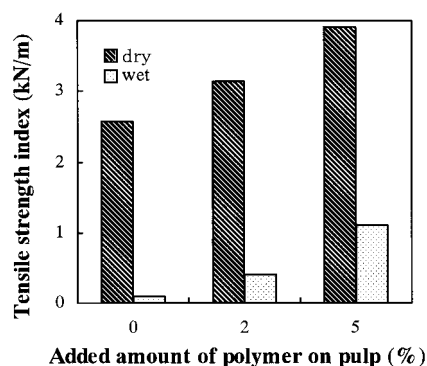


Figure 3 Dry and wet strength of sheets vs. added amount of PGS on pulps. PAAM : PGS = 1 : 10 (w/w).

tent of the polymer was determined by the HCl–dioxane titration method.¹⁴ The data showed that 95% of the glycidyl groups in GMA remained (0.38 eq/100 g) after the polymerization. This suggests that very little hydrolysis of the glycidyl group takes place during polymerization.

Because the polymer containing the glycidyl groups can react with materials containing amino groups, polyallylamine (PAAM) was used together with PGS to make crosslinkings. Hydroxyl groups and carboxyl groups of fibers are also capable of reacting with the glycidyl groups. The reaction occurs relatively easily in the case of the amine–glycidyl system. It needs high temperature (200°C) to make hydroxyl–glycidyl and carboxyl–glycidyl reaction.¹⁵ Generally, hydroxyl groups accelerate an amine–glycidyl reaction markedly instead of participation in the reaction.¹⁶ In the case of carboxyl groups, the dissociated form (COO^-) of COOH , however, was found to react with the glycidyl group quite easier.^{9,15} Therefore, the paper making was carried out at pH 7.5, which converted parts of COOH to the COO^- form.¹⁷ The COO^- groups in the pulps would be expected to react with the glycidyl groups under curing temperature (105°C).

At first, PAAM was chosen as a retention aid for PGS emulsion. It was found after preliminary experiments that the paper exhibited higher strength improvement when the ratio of PAAM to PGS was 1 : 10 (w/w). Larger quantities of PAAM would exhaust glycidyl groups and reduce the interactions with fibers. Figure 3 shows some results on the improvement of paper dry and wet strength. When PAAM 0.5% and PGS 5% were added into the pulp, sheet dry strength was increased at the level of 50% and wet strength retention reached 40% (based on untreated paper).

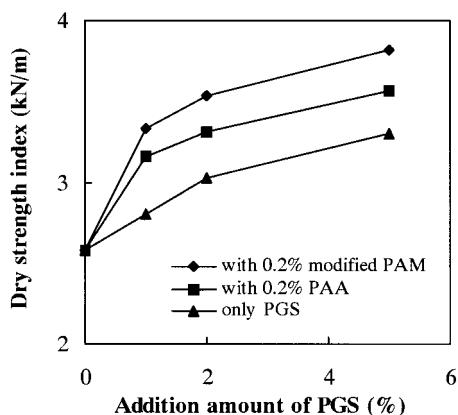


Figure 4 Effects of PAA or modified PAM together with PGS on paper dry-strength improvement (PDADMAC 0.2% as retention aid).

To confirm the effect of carboxyl groups on paper-strength improvement, polyacrylic acid (PAA) was selected to react with PGS in paper making using polydiallyl-dimethylammonium chloride (PDADMAC) as a retention aid. The results are shown in Figure 4 and Figure 5. Contrasting to the sheet with only PGS, the sheet with 0.2% PAA achieved higher dry- and wet-strength improvement. This indicates that a small amount of carboxylic compounds can give considerable improvement on paper strength when PGS is applied together. However, the wet-strength retention of the sheet with PAA and PGS is still not satisfied (25% based on dry strength of untreated sheet).

Then a polymer with amino and carboxyl groups was prepared by modification of PAM. A part of the amide groups of PAM was converted

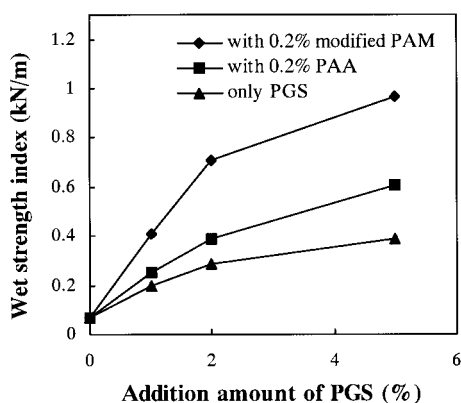


Figure 5 Effects of PAA or modified PAM together with PGS on paper wet-strength improvement (PDADMAC 0.2% as retention aid).

Table II Sizing Degree of the Papers Determined by Stöckigt Test

Sheets (60 g/m ²)	Sizing Degree, s
Original pulp	0
Original pulp with 0.2% PAAm and 2% PGS	2.0
CMP5 with 0.2% PAAm and 2% PGS	5.5

into carboxyl groups by alkaline hydrolysis,^{18,19} and a part was converted into amino groups by the Hofmann reaction.²⁰ The resulting polymer contained an amino group 28.5 mol % and a carboxyl group 21.3 mol %. The effect of the amphoteric PAM on paper dry- and wet-strength improvement is shown in Figures 4 and 5. When the modified PAM (0.2%) was added together with PGS (2%) using PDADMAC (0.2%) as a retention aid, for example, the paper dry strength was increased at the level of 40% and wet-strength retention reached 30% (based on untreated paper).

It is known that hydrophobic crosslinkings made between polymers and fibers can lead to strong and permanent paper wet-strength improvement. To provide adequate carboxyl groups of fibers for reaction, several kinds of carboxymethylated pulps (CMP) were prepared according to the conditions listed in Table I.

CMP papers showed higher hydrophobic ability than original pulp paper after reacting with PGS. Table II shows the sizing degree of the papers determined by the stöckigt test. The sizing degree is expressed in penetration time of water solution through a z-direction of a sheet. The sizing degree of CMP paper is higher than that of the original pulp paper when the same amount of PGS was used as a wet-strength agent. This indicates that carboxyl groups of pulp react with glycidyl groups of the copolymer to form linkages that resist water. This mechanism contributes to reinforce paper wet strength.

The effect of CMPs added with PAAm and PGS on the dry and wet strength of sheets is given in Figures 6 and 7. The dry strength of CMP paper could be increased at the level of about 65%, and the wet-strength retention of CMP paper could reach 45% (based on untreated paper).

CMP5 was used to mix with original pulp at different ratios, and the effect on the improvement of paper strength after treatment with 2% PGS was investigated. The results are given in

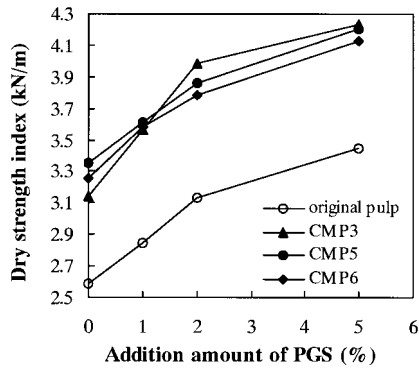


Figure 6 Dry-strength improvement of different pulps by adding with 0.2% PAAm and PGS.

Figures 8 and 9. When content of CMP in the pulp increased, the sheet showed higher dry and wet strength. The result gave good agreement that carboxyl groups of fibers affected the performance of glycidyl groups during the curing process. The CMPs can be mixed with other pulps as furnish material to achieve higher paper strength by using of PGS as a strength additive. The relationships between PGS, PAAm, and fibers of CMP and original pulp are in a study process.

Comparison of PGS resin with other wet-strength agents has not been made using the same pulp. Because PAE resin is the most common wet strength agent at present, and it can provide higher wet strength than UF and MF resins, wet strength data of PAE taken from a literature²¹ was used to compare with the PGS resin. When unbleached softwood kraft pulp was treated with 2% of PAE resin, the sheet wet strength reached 30% in the case of high MW PAE and only 10% in the case of low MW PAE (based on the dry strength of untreated paper).

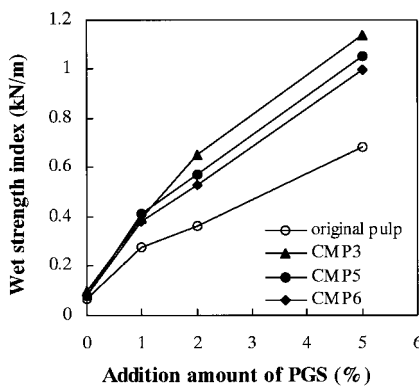


Figure 7 Wet-strength improvement of different pulps by adding with 0.2% PAAm and PGS.

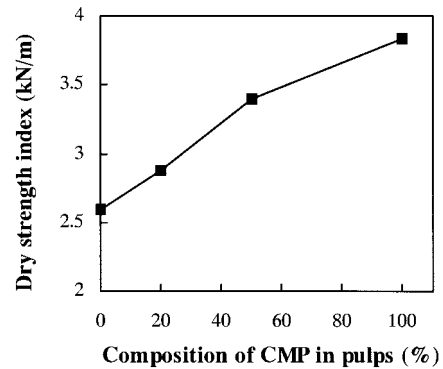


Figure 8 Relationship between content of CMP5 in pulp and paper dry-strength improvement (with 0.2% PAAm and 2% PGS addition).

This means that the effectiveness of PGS on paper wet strength is close to that of PAE. Considering the drawbacks of PAE, such as AOX discharging and storage difficulty, the suggested PGS resin has an advantage to be further studied and applied.

CONCLUSIONS

The copolymer of glycidyl methacrylate and styrene (PGS) was synthesized. There was little hydrolysis of glycidyl groups during the emulsion polymerization. PGS contains glycidyl groups, so it can react with other polymers containing nucleophilic groups to form crosslinkings between the polymers. PGS can also react with the carboxyl groups of fibers to form crosslinkings that connect the fibers. Result shows that PGS has significant effect on paper dry- and wet-strength

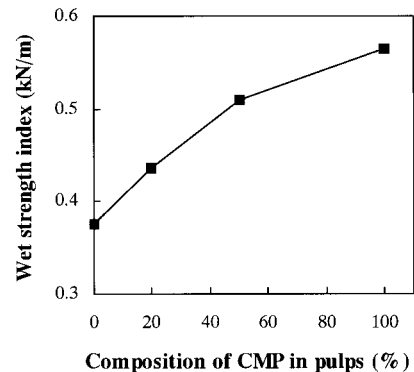


Figure 9 Relationship between content of CMP5 in pulp and paper wet-strength improvement (with 0.2% PAAm and 2% PGS addition).

improvement by using it with PAAm, PAA, or modified PAM.

Partially carboxymethylated pulps (CMP) were prepared and compared with original pulp in paper-strength improvement after treated with the PGS resin. Results showed that CMPs gave higher paper dry- and wet-strength improvement than original pulp by using of PGS as a paper-strength agent. This confirms that carboxyl groups of fibers can react with glycidyl groups of PGS during curing to improve paper strength.

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