

Study on Application of Block Copolymers Composed of Poly(vinyl Alcohol) and Polyacrylamide to Paper Sizing

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SYNOPSIS

Block copolymers of poly(vinyl alcohol) (PVA) and polyacrylamide (PAAm) were investigated as paper additives. The mixture of both homopolymers in aqueous solution caused phase separation, which indicated incompatibility. The block copolymers were soluble in water without macrophase separation. In the case of surface sizing to paper, PVA-b-PAAm as well as PAAm afforded stiffness to paper, whereas PVA could not. In the case of internal sizing, the block copolymers with anionically modified PAAm revealed excellent improvement in paper properties, whereas PAAm made the tearing strength worse. Brittle polymers such as PAAm appear to afford stiffness to paper, but also make the paper brittle. PVA that is a tough polymer due to high crystallinity and low glass transition temperature can afford toughness to paper, at the expense of stiffness. The block copolymers seem to retain the desirable properties of each simultaneously. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Poly(vinyl alcohol) (PVA) and polyacrylamide (PAAm) are utilized in the paper industry to improve barrier and mechanical properties. Both polymers are added to paper via different methods: PVA being added in the surface sizing with the size press after sheet forming, and PAAm being done in the internal sizing during the sheet forming. There are also different contributions of both polymers to improve paper properties. PVA does not increase paper stiffness but affords barrier properties against oil and air to a great extent, and against water to some extent. Increases in paper mechanical properties, including tearing strength, are remarkable in this case. On the contrary, PAAm increases paper stiffness to a great extent, but affords poor barrier properties. Increases in mechanical properties excluding tearing strength are also remarkable in this case.

The authors have reported on the synthesis and basic properties of A-B type block copolymers such as PVA-b-PAAm.^{1,2} PVA and PAAm were found not to be compatible with each other, which resulted

in phase separation in aqueous solution, while the aqueous solution of the block copolymer was found to be almost homogeneous. This enabled us to use the block copolymer as a paper additive. In this article, surface sizing as well as internal sizing will be dealt with in relation to the paper properties mentioned above.

EXPERIMENTAL

Materials

PVA-117 (Kuraray Co., degree of polymerization 1700, degree of hydrolysis 98.5%) was used after removing sodium acetate with methanol in a Soxhlet apparatus. PVA containing a small amount of trihydroxysilyl (Si-PVA) was prepared by copolymerizing vinyl acetate (VAc) with vinyltrimethoxysilane followed by the usual alkaline methanolysis.^{3,4} Cationic PVA, P(VA/QAPM), was prepared by copolymerizing VAc with trimethyl[(3-methacryloylamino)propyl]ammonium chloride (QAPM), followed by the usual alkaline hydrolysis^{5,6} (QAPM content being 0.5 mol %). The alternating copolymer of isobutene and maleic anhydride (Isobam-104, Kuraray Co., degree of polymerization 400, degree of neutralization with ammonia, 80%) was used

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without further purification. Anionically modified polyacrylamides, PAAm-2 and PAAm-5, were commercial products (Arakawa Chemicals, Polymeriset-500A and Polystron-117, respectively) and used as received. Modified (oxidized) starch, a commercial product (Japan Maize Products Co., MS-3800), was used as received. PAAm homopolymer (PAAm-1), anionic PAAm (PAAm-3), and cationic PAAm (PAAm-4) were synthesized by polymerizing acrylamide (AAM) in aqueous solution in the absence of comonomer, in the presence of acrylic acid (AA, 5 wt %/total monomers), and in the presence of QAPM (3 wt %/total monomers), respectively, where concentrations of monomers were 20 wt % and a redox initiator system composed of 3-mercaptopropanoic acid and potassium bromate was used.⁷ Colloidal silica (CS) was used as received (Nissan Chemicals Co., Snowtex-SN-O, particle diameter 20–30 nm). CP grade aluminum sulfate with 14–18 crystalline water was used as received.

Block Copolymerization

PVA with a thiol end group (PVA-SH) was prepared by polymerizing VAc in the presence of thioacetic acid, followed by the usual alkaline hydrolysis.¹ The resulting PVA-SH (degree of polymerization 370, degree of hydrolysis 99%, thiol content 6.21×10^{-5} eq/g) was dissolved in water to make the concentration of resulting copolymers 15%. The aqueous solutions were adjusted to pH 3 with sulfuric acid, and the prescribed amounts of AAM and other comonomers were added. After deaeration with nitrogen gas, the solutions were heated to 70°C, and potassium bromate aqueous solution was added continuously for 90 min, followed by continued polymerization for another 90 min. The molar ratio of thiol to potassium bromate was 1 : 1. The conversions of AAM and other comonomers were over 99%, and the aqueous solutions were used without further purification. The block copolymers appeared to contain small amounts of homopolymers, i.e., PVA and PAAm [or P(AAM/other comonomer)]. According to the calculations and the initiation mechanism described in previous articles,^{1,2} the amounts seem to be less than 10%, although they have not yet been analytically determined.

Sizing Tests

The surface sizing tests were carried out using a size-press machine (Kumagai Riki Kogyo Co., Ltd.). Papers were size-pressed with aqueous polymer solutions at 50°C, 10 kg/cm² pressure, and 60 m/min

speed, followed by drying at 105°C for 1 min. The amounts of absorbed polymers were calculated from the absorbed amounts of the aqueous solutions.

The internal sizing tests were carried out per the following procedure. Aluminum sulfate and 1% aqueous solutions of polymers were added successively to slurries of 3% pulp in a homogenizer at 1000 rpm. The resulting mixtures were put into a sheet-forming machine (Kumagai Riki Kogyo Co., Ltd.) and diluted to 1/17 concentration. After 10 s, the liquid portions were dropped out. The sheets were then roll-pressed, followed by pressing at 3.5 kg/cm² for 5 min and drying at 110°C for 3 min.

The amounts of polymers adsorbed onto the pulp were measured in other experiments, where 1% pulp slurry and 1% polymer solution were mixed together with a stirrer for 10 min, and the amounts of polymers in serums were measured gravimetrically after separation of the serums from the mixtures.

Measurement of Paper Properties

All measurements were carried out at 20°C and 65% RH. Stiffness was measured according to TAPPI T 451 (Clark stiffness). Oil absorptivity was measured by using polybutene as an oil (JIS P 8130). Surface strength (IGT pick strength) was measured according to JIS P 8129 (corresponding to TAPPI UM 591). Thickness, basis weight, tensile strength, and breaking length were measured according to JIS P 8118, 8124, 8113, and 8113, respectively (corresponding to TAPPI T 551, T 410, T 494, respectively). Young's modulus was obtained in the experiment via JIS P 8113. Bursting strength was measured according to TAPPI T 403 and expressed as burst factor [bursting strength (kgf/cm²)/basis weight (g/m²)]. Tearing strength was measured according to TAPPI T 441, and expressed as Elmendorf factor [tearing strength (g) × 100/basis weight (g/m²)]. Resistance to folding (folding endurance) was measured by using an MIT machine (TAPPI T 511). Interfiber bond strength (Z-direction tensile strength) was measured according to TAPPI UM 403.

RESULTS AND DISCUSSION

In the paper industry, PVA has been utilized as a material to both afford barrier properties and increase mechanical properties. It is, however, difficult to increase paper stiffness with PVA. Among various attempts to improve the stiffness, addition of poly(isobutene/maleic anhydride) to PVA has been

Table I Effect of Various Polymers Added onto Paper via Surface Sizing on Clark Paper Stiffness^a

Polymer	Coated Weight (g/m ²)	Clark Stiffness (cm)
None	—	20.1
PVA-117	1.84	21.1
Si-PVA ^b + CS ^c	1.17	21.4
Si-PVA ^b + CS ^{c,d}	1.97	21.8
PVA-117 + Isobam-104 (100/100) ^e	1.79	22.0
PVA-117 + Glyoxal (100/50) ^e	1.55	22.2
PAAm-1	1.25	22.1
PVA-b-PAAm (100/100) ^e	1.61	22.2
PVA-117 + PAAm-1 (100/100) ^e	1.48	21.6

^a Surface sizing; paper: high quality paper (Jujiyo Paper Co., 84 g/m²); polymer: 6% aqueous solution.

^b PVA containing a small amount of trihydroxysilyl unit.

^c Colloidal silica.

^d Aqueous solution (9%) was used.

^e Numbers in parentheses denote weight ratio.

the best method.⁸ An alternative is to add glyoxal to PVA.⁸ Both methods are believed to make PVA harder by crosslinking the molecules, but these methods bring about unfavorable decreases in other properties.

At first, the effect of the addition of the block copolymer, PVA-b-PAAm, on the paper stiffness was investigated. In Table I are listed Clark paper stiffness (expressed as critical length), obtained via surface sizing by using various polymers as additives.

In the case of ordinary PVA (PVA-117) the increase in stiffness is 1 point, while in the both cases mentioned above, the increases are 2.0 to 2.2 points. A mixture of ordinary PVA with colloidal silica that had given hard films in a previous article⁴ increased the stiffness to some extent. PAAm increased the stiffness 2 points, and the block copolymer had a similar effect. A mixture of PAAm with PVA increased the stiffness to some extent, but in this case, unfavorable phase separation took place in the aqueous solution.

Other paper properties, including the stiffness, were investigated by varying the composition of the PAAm portion in the block copolymer, as shown in Table II. The results for modified starch, commonly utilized in the paper industry, are listed for comparison. In this case, polymer concentrations were twice those of the other cases, since the capability of modified starch to enhance paper properties is known to be less than half that of PVA.⁸

As is clear from Table II, PVA as well as modified starch increased surface strength (IGT pick strength), barrier to oil permeation (oil absorp-

Table II Effect of Various Polymers Added onto Paper via Surface Sizing on Some Properties of Paper^a

Polymer	Coated wt (g/m ²)	IGT Pick Strength (cm/s)	Oil Absorptivity (s)	Tensile Strength (kg/15 mm)	Clark Stiffness (cm)
None	—	100	4.5	2.27	24.0
Modified starch ^b	0.62	149	6.5	2.12	24.5
	1.72	216	11.8	2.88	24.5
PVA-117	0.35	166	8.5	2.53	24.2
	1.05	283	11.6	2.68	24.1
PAAm-2 ^c	0.38	145	6.0	2.49	24.8
	0.98	238	6.0	2.78	25.0
PVA-b-PAAm ^d	0.35	155	5.5	2.60	24.2
	0.96	251	5.5	2.66	25.0
PVA-b-P(AAm/AA) ^e	0.36	166	6.0	2.54	25.0
	0.93	250	8.0	2.39	24.7
PVA-b-P(AAm/QAPM) ^f	0.37	158	5.0	2.01	24.8
	0.98	232	7.2	2.91	25.0

^a Surface sizing; paper: raw paper for coated paper (Hokuetsu Paper Mills); polymer concentration in water: 2% for upper and 4% for lower experiments (4 and 8%, respectively, in the case of modified starch).

^b Commercial product (MS-3800).

^c Commercial product (Polymerset-500A).

^d 100/100 (wt ratio).

^e 100/95/5 (wt ratio).

^f 100/97/3 (wt ratio).

Table III Capability of Adsorption of Various Polymers onto Pulp in Aqueous Slurries

Polymer	Adsorbed Polymer (%)		
	Without Al ₂ (SO ₄) ₃	With Al ₂ (SO ₄) ₃	
		1%/pulp	2%/pulp
PVA-117	6	0	—
P(VA/QAPM) (99.7/0.3) ^a	91	100	—
PAAm-1 (nonionic)	5	50	—
PAAm-3 (anionic)	6	63	84
PAAm-4 (cationic)	40	—	—
PVA-b-PAAm (100/100)	1	13	—
PVA-b-P(AAm/AA) (100/95/5)	24	51	—
PVA-b-P(AAm/QAPM) (100/97/3)	69	97	—

^a Numbers in parentheses denote weight ratio.

tivity), and tensile strength, but showed only a slight stiffness increase. PAAm showed better stiffness, similar IGT pick strength, and tensile strength, but lower barrier to oil permeation compared with PVA. In the case of the block copolymers, results were similar to PAAm.

Internal sizing experiments were also carried out. Since added polymer should adsorb or deposit onto paper during sheet formation with internal sizing, the capability of polymer adsorption onto pulp in aqueous slurries was first investigated, as shown in Table III. PVA and PVA-b-PAAm without ionic groups did not substantially adsorb onto paper. Polymers with cationic groups, P(VA/QAPM), PAAm-4, and PVA-b-P(AAm/QAPM), adsorbed onto paper both with and without aluminum sulfate. Polymers with anionic groups, PAAm-3 and PVA-b-P(AAm/AA), adsorbed onto paper to a markedly greater extent in the presence of aluminum sulfate. With the anionic (PAAm-3) polymer, the amount

of adsorbed polymer increased with increase in salt concentration from 1 to 2%.

It is well known that cationic polymers adsorb onto substances having negative ζ -potential such as pulp in an aqueous slurry, and that in the presence of aluminum sulfate, anionic polymers adsorb onto the substances by ionic interaction. The results in Table III can be explained by these facts.

The internal sizing tests themselves were carried out using the polymers listed in Table IV. Table V lists the paper properties. As expected, there are no substantial property improvements from addition of polymers without anionic groups, except for PAAm-1, which showed reasonable adsorption capability in the presence of aluminum sulfate (Table III). Such adsorption might be due to carboxyl groups at the polymer ends introduced by the initiator system. In the case of anionic PAAm (PAAm-5) improvements in tensile strength, breaking length, resistance to burst (burst factor), folding en-

Table IV Polymers Used in Internal Sizing Experiments

No.	Polymers	Composition of Copolymer (wt ratio)	Degree of Polymerization of PVA
1	(Blank)	—	—
2	PVA-117	—	1700
3	P(VA/QAPM)	99.7/0.3	1700
4	PAAm-1	—	—
5	PAAm-5	—	—
6	PVA-b-PAAm	100/100	370
7	PVA-b-P(AAm/AA)	100/95/5	370
8	PVA-b-P(AAm/QAPM)	100/97/3	370

Table V Effect of Various Polymers as Internal Sizing Agents on Properties of Paper^a

No.	Thickness (mm)	Basis Wt (g/ m ²)	Tensile Strength (kg/15 mm)	Elongation (%)	Breaking Length (km)	Burst Factor	Elmendorf Factor	Fold Endurance (time)	Z-	IGT Pick Strength (cm/s)
									Direct. Tensile Strength (kg · cm)	
1	0.130	65.5	4.64	3.8	4.73	3.55	63.3	170	1.41	50
2	0.134	69.0	5.07	3.9	4.90	3.57	63.1	330	1.42	60
3	0.134	71.2	5.87	3.8	5.50	4.13	62.0	830	1.83	110
4	0.135	73.8	5.13	3.5	4.63	3.20	72.4	260	1.51	40
5	0.132	71.1	6.87	4.4	6.44	5.24	57.8	1550	2.73	170
6	0.125	59.7	4.41	3.6	4.92	3.37	57.3	120	1.38	60
7	0.139	75.9	7.01	4.1	6.15	4.74	64.8	1460	2.39	190
8	0.126	62.7	4.97	3.8	5.29	3.83	68.5	360	1.75	105

^a Pulp: NUKP (needle-leaves tree, unbleached Kraft pulp); CSF (Canadian Standard Freeness) 450 mL; polymer: 1%/pulp; aluminum sulfate; 3%/pulp.

duration, Z-direction tensile strength, and IGT pick strength were remarkable. In this case, a decrease only in tearing strength (Elmendorf factor) was observed, which will be described later. Block copolymer composed of PVA and P(AAm/AA) revealed almost the same level of improvement in the paper properties as anionic PAAm (PAAm-5) by itself, except for the reverse tendency in the tearing strength. PVA with cationic groups, P(VA/QAPM) showed marginal ability to improve the paper properties, notwithstanding the excellent capability of adsorption to paper, as shown in Table III. This tendency

has been already reported.^{5,6} The block copolymer with cationic groups in the PAAm portion, PVA-b-P(AAm/QAPM), revealed the same tendency as the cationic P(VA/QAPM).

The effect of A-B block copolymer composition on the internal sizing was investigated by changing the weight of the B portion, while keeping the weight of the A portion (PVA) constant at 100 parts. Table VI lists the results, where the paper properties are shown as relative values compared to the data of the control material (blank), without polymers, taken to be 100 in each case.

Table VI Effect of Composition of B Portion in A-B Block Copolymer as Internal Sizing on Properties of Paper^a

Composition of B in A-B Block Copolymer			Relative Properties of Paper ^d					
			Young's Modulus	Burst Factor	Elmendorf Factor	Folding Endurance	Z-Dir. Tensile Strength	IGT Pick Strength
(Blank)			100	100	100	100	100	100
(PAAm-5 ^{b,c})			—	147	91	890	194	340
47.5	2.5	—	143	128	97	830	176	190
95	5 ^c	—	—	134	102	840	169	380
190	10	—	161	147	97	1280	228	350
48.5	—	1.5 ^d	125	115	110	340	103	130
97	—	3 ^d	144	129	108	380	106	154
194	—	6 ^d	161	131	105	450	111	194

^a Block copolymer: portion A being 100 parts of PVA (degree of polymerization 370); pulp: NUKP, CSF 450 mL; polymer: 1%/pulp; aluminum sulfate: 3% pulp.

^b Commercial product.

^c The same data in Table V.

^d Without aluminum sulfate.

^e The data of blank are regarded as 100.

In the cases of the block copolymers with anionic (AA) groups in the PAAM, paper properties are improved, with increasing weight of the PAAM portion, with the exception of the tearing strength (Elmendorf factor). In the case of the block copolymers with cationic groups in the PAAM, the same tendencies can be observed, although the degrees of increase were less.

In the internal sizing experiments in Tables V and VI, polymers were added at 1% concentration. The effect of polymer concentration was investigated using anionically modified PAAM (PAAM-2) and two kinds of block copolymers that contain different weight ratios of A to B, and have anionic groups in the B-portion. Figure 1 shows the effect of polymer concentration in the internal sizing on breaking length, burst factor, and Z-tensile strength. Figure 2 shows folding endurance, Elmendorf factor, and IGT pick strength.

Among the three kinds of polymers, there were similar improvements in paper properties, with the exception of the Elmendorf factor. In the case of the PAAM, an increase in the amount of PAAM

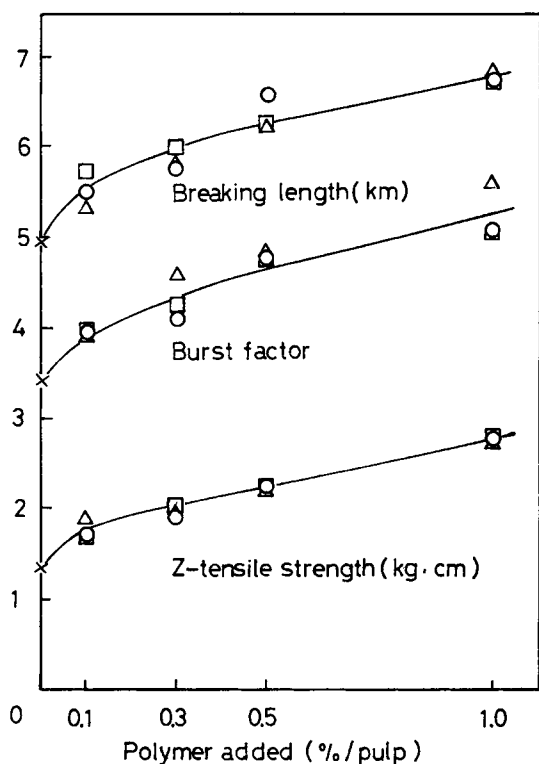


Figure 1 Effect of polymer concentration in the internal sizing on the paper properties. Pulp: NUKP, CSF 450 mL; aluminum sulfate: 2%/pulp. (○) Anionically modified PAAM (PAAM-5); (□) PVA-b-P(AAm/AA) (100/95/5); (△) PVA-b-P(AAm/AA) (100/190/10).

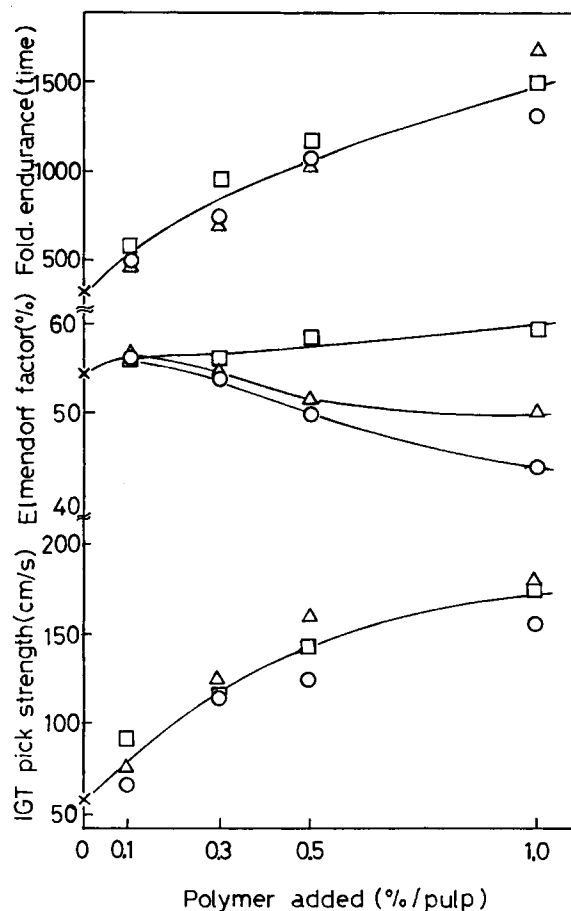


Figure 2 Effect of polymer concentration in the internal sizing on the paper properties. Conditions the same as in Table I.

lowered the tearing strength, for the most part, with the exception of the 0.1% addition. On the contrary, the block copolymer containing 50 wt % of PVA increased the tearing strength with increasing amount of polymer. In the case of the block copolymer with 33% of PVA, the tearing strength showed intermediate behavior compared with the other two polymers.

To clarify the behavior described above, the mechanical properties of the added polymers were measured. Films were formed by casting the aqueous solutions of the polymers without pulp and aluminum sulfate. Table VII shows the results.

As clearly shown in Table VII, the elongation of PVA film was very large, whereas that of PAAM film was very small. (Actually the elongation of PAAM film could not be measured due to the brittleness of the film.) The blend film of the both polymers could not be formed because of the lack of solution homogeneity. In the cases of the block copolymers, an increase in the PAAM portion made

Table VII Mechanical Properties of Block Copolymer Films^a

Polymer	Composition (wt ratio)	Young's Modulus (kg/mm ²)	Yield Strength (kg/mm ²)	Elongation (%)
PVA ^b	PVA	46	3.72	200
PVA-b-P(AAm/AA)	100/47.5/2.5	58	3.29	158
	100/95/5	108	4.23	30
	100/190/10	117	4.32	8
	100/48.5/1.5	81	3.37	136
PVA-b-P(AAm/QAPM)	100/97/3	116	4.40	43
	100/194/6	148	4.96	28
	PAAm	c	c	c
PAAm-1	PAAm	c	c	c
PVA ^b + PAAm-1	100/100	d	d	d

^a Film formation: cast from 15% aqueous solutions of polymers: measurement at 20°C, 65% RH.

^b PVA-SH (degree of polymerization 370) used for the block copolymerization.

^c Too brittle to be measured.

^d Film formation poor due to phase separation.

the films stiffer, that is, Young's modulus was higher and elongation was lower. This phenomenon can be observed both in anionically and cationically modified PAAms in the block copolymers. Increase in the yield strength with increase in the PAAm portion may be due to the exceptionally low degree of polymerization of the PVA used (DP = 370).

The mechanical property behavior of both polymers comes from the fact that PVA is a crystalline polymer while PAAm is amorphous, and that the glass transition temperature of PVA is lowered from 85°C to below room temperature by moisture absorption, while that of PAAm is much higher than room temperature.^{9,10} Such properties allow PAAm to improve paper stiffness, while the properties of lower Young's modulus and larger elongation revealed in PVA film can not act in a similar manner.

Since stiff polymers with high Young's modulus and low elongation have low toughness, they show diminished resistance to tearing stress. This is probably why PAAm could not impart tearing strength to paper, especially when large amounts were added, as shown in Figure 2. It should be worth noting that the block copolymers composed of PVA and PAAm containing a small amount of anionic comonomer improve both stiffness and resistance against tearing simultaneously. In other words, this

must be characteristic of block copolymers, where both polymers are incompatible with each other.

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