A new sizing agent: styrene-maleic anhydride copolymer with alum or iron mordants

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ABSTRACT

Alkali-soluble styrene-maleic anhydride copolymers (SMA) were found to be good sizing agents on unbleached Douglas-fir kraft pulp and unbleached thermomechanical pulp (TMP) when used with ferrous chloride or alum as mordants. Three SMAs with different molecular weights and maleic anhydride contents were tested as internal sizing agents for both bleached and unbleached pulps. All three polymers gave good sizing to the unbleached pulps. None showed any significant sizing effect on bleached pulps. No dependence upon polymer molecular weight or maleic anhydride content was observed. Rosin sizing showed approximately the same breaking length and burst index regardless of mordant. SMA sized unbleached Douglas-fir kraft pulp with ferrous chloride or alum as mordant gave increases of 49–59% in breaking length and 51–65% in burst index when compared to rosin sized paper at the same conditions. Brightness was greatly decreased when ferrous chloride was used as mordant.

Application:

SMA copolymers show considerable potential as high strength internal sizing agents for paper.

SIZING AGENTS HAVE BECOME an important research concern as more companies convert to neutral and alkaline papermaking. While the mechanism of internal sizing is not completely understood, it is clear that the sizing process alters the surface properties of the paper pulp, resulting in greater resistance to water penetration. This is accomplished in rosin sizing by precipitating the rosin acid with alum. In alkaline systems, emulsions of alkyl ketene dimer (AKD) and alkyl succinic anhydride (ASA) are retained on the fiber surface, presumably forming ester bonds to fiber hydroxyl groups *(1, 2)*. In both cases, the surface of the fiber is effectively covered with a hydrophobic film which resists wetting by liquid water. A different type of chemical system that also shows a sizing effect is presented here. Maleic anhydride (MA) modified styrene copolymer (SMA) has previously been used as a sizing agent, mostly for surface sizing *(3)*. Typically the salt form of the SMA is employed. The anhydride group on the polymer is hydrolyzed with an ammonium or alkali hydroxide. Alum or zirconium is often employed to precipitate the SMA and create the sizing effect.

SMA copolymers are relatively inexpensive and commercially available in a variety of molecular weights and styrene/maleic anhydride ratios. The SMA copolymers chosen for these experiments are not soluble in water and are solids at room temperature. However, when saponified with alkaline compounds, they are water soluble, depending upon the pH, molecular weight, MA/styrene ratio, concentration, and temperature. The SMA copolymers used here had molecular weights ranging from 1700 to 50,000, and maleic hydride contents ranging from 25% to 50%. **Figure 1** shows the molecular structure of SMA, which has adjacent -COOH groups in the polymer repeat unit.

Two mordants were chosen for these studies: alum and Fe(II). These have previously been reported to be good mordants for rosin *(4, 5)* . The pH is very important because alum and ferrous ions form oxo- and hydroxo-complexes in water solution and the nature and extent of these complexes is pH dependent *(6)*.

The objective of this study was to determine the feasibility of using SMA copolymers in conjunction with an iron or aluminum mordant as internal sizing agents for paper pulp.

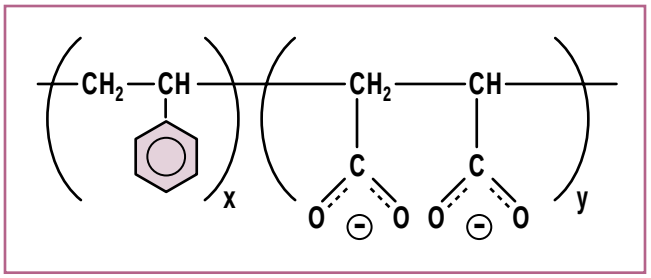
RESULTS AND DISCUSSION

Polymer type

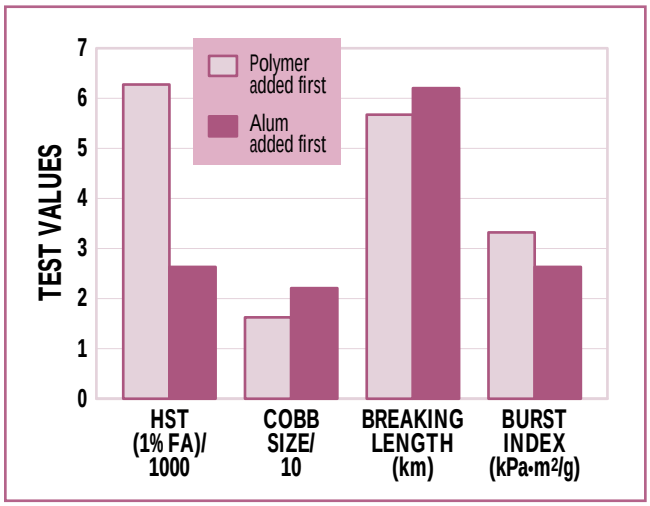
The SMA copolymers (described under the heading "Experimental procedure") differed in molecular weight and maleic anhydride content. All these copolymers gave similar results on unbleached Douglas-fir kraft pulp and TMP (**Tables I and II**), suggesting that, within the limits of these experiments, the molecular weight and MA content did not strongly relate to sizing performance. However, all the HST values were high. A relationship between molecular weight and sizing might become apparent at lower polymer concentrations. The polymers showed greater sizing in unbleached Douglas-fir kraft pulp than in TMP.

Bleached vs. unbleached pulps

Table III indicates that the bleached pulps were not sized by the SMA. This result suggests that the sizing effect with SMA involves the lignin or other components



(above) 1. Chemical structure of SMA copolymer



(right) 2. Order of addition experiment, Douglas-fir kraft pulp, 2% polymer 1 and 2% alum as mordant, both measured as % dry pulp, pH = 4.5

(such as the weak acid content) of the wood, which were removed or chemically modified during the bleaching process. The ability of lignin to complex with metal ions is well known *(7)*. A recent report suggests that coordinate bonding between Fe(III)/Fe(II) and guaiacol units may be present. Another report described the conformation of several Fe^{3+}/Fe^{2+}-lignin complexes *(8)*. The results with SMA copolymers contrasted sharply with those of rosin acids and alum, where good sizing was obtained on bleached pulps. These data support the hypothesis that a complex precipitate is being formed wherein the mordant ions, lignin component of the pulp, and the SMA copolymer all interact. The inability of the SMA copolymers to provide sizing in the absence of lignin suggests a complicated interaction among these three components.

Referring to Table II again, we notice that the ferrous chloride performed well compared to alum in the HST (1% formic acid) test on TMP. This result agrees with a previous report *(1)*. The iron precipitate appears to be more resistant to acid dissolution than that precipitated by alum. This suggests the possibility of strong bonding between the Fe(II) ion and the lignin-SMA complex.

Figure 2 indicates that the most effective order of addition of polymer and mordant is polymer first. This is the same order observed for alum and rosin under most conditions. It is interesting that the strength properties were not as adversely affected as the sizing properties. This might indicate that the order of addition affects the film-forming properties of the precipitate but has less effect on the interfiber adhesion, which is increased by the presence of SMA copolymer.

Polymer concentration

The effect of increasing polymer 1 concentration is shown in **Table IV**. No sizing was observed with SMA copolymers in the absence of mordants, and, of course, no sizing was observed with mordant alone. In addition, ferrous chloride outperformed alum as a mordant in unbleached Douglas-fir kraft pulp. While rosin sizing was numerically superior to SMA sizing with either mordant, all compounds gave good sizing to the test papers. The ferrous mordant significantly reduced the brightness of the final sheets. They were deep gray in color.

pH

Competing effects produced an optimum pH for sizing (**Figs. 3 and 4**). In a separate experiment, it was observed that a 2% saponified solution of polymer 1 began to precipitate (the solution became cloudy) as the pH was lowered below about 4. This was due to the formation of acid groups on the polymer. The acidified polymer was insoluble in water. Only the hydrolyzed, or salt, form was soluble. Thus the higher the pH, the more soluble the polymer became, within the ranges of interest here. On the other hand, higher pH should reduce the solubility of the mordant. If the pH is raised above about 5, we would expect alum to precipitate as a mixture of complex aluminum hydroxides. We also expect ferrous ion to go through an analogous transition, but at a higher pH. At the concentrations of interest here, the ferrous solution should be stable to a pH of about 7.5. Above that, ferrous hydroxide should precipitate *(6)*.

The behavior of alum in the SMA system was similar to that in the rosin system. Optimum performance was observed at a pH of 4.5. The ferrous ion was optimized at the higher pH of 6.5. Brightness was relatively constant throughout the pH range observed for both mordants. The ability to utilize ferrous ion as a mordant in the SMA system allows the use of pH's more neutral than alum mordants. This is an advantage for the iron-SMA copolymer sizing system.

Mordant	Amount added, % dry pulp	pH	Polymer type*	Amount added, % dry pulp	HST Neutral	HST (1% FA)	Cobb Size, g/m^2	Brightness, %
Alum	2.0	4.5	1	1.0	3,383	480	32.1	17.8
Alum	2.0	4.5	1	2.0	4,000	630	18.0	17.5
Alum	2.0	4.5	1	2.5	9,258	1197	20.6	17.1
Alum	2.0	4.5	2	1.0	5,608	523	24.3	18.3
Alum	2.0	4.5	2	2.5	9,430	1023	21.7	17.3
Alum	2.0	4.5	3	1.0	4,235	537	26.9	17.4
Alum	2.0	4.5	3	2.5	6,920	1097	17.5	17.5
Alum	2.0	4.5	Rosin	2.0	>5,000	1100	19.3	19.0

*See Experimental Procedure section

I. Sizing of unbleached Douglas-fir kraft pulp by different polymers

Mordant	Amount added, % dry pulp	pH	Polymer type*	Amount added, % dry pulp	HST (Neutral)	HST (1% FA)	Cobb Size, g/m^2	Brightness, %
$FeCl_2$	2.5	3.5	1	1.0	194	73	33.4	27.3
$FeCl_2$	2.5	3.5	1	2.5	12,000	2480	18.3	31.2
$FeCl_2$	2.5	3.5	2	1.0	1,240	263	27.8	28.6
$FeCl_2$	2.5	3.5	2	2.5	>12,000	8648	15.8	28.5
$FeCl_2$	2.5	3.5	3	1.0	139	102	35.4	28.8
$FeCl_2$	2.5	3.5	3	2.5	>14,000	5350	18.3	27.6
Alum	2.0	4.5	1	2.0	270	68	34.6	42.8

*See Experimental Procedure section

II. Sizing of TMP by different SMA polymers

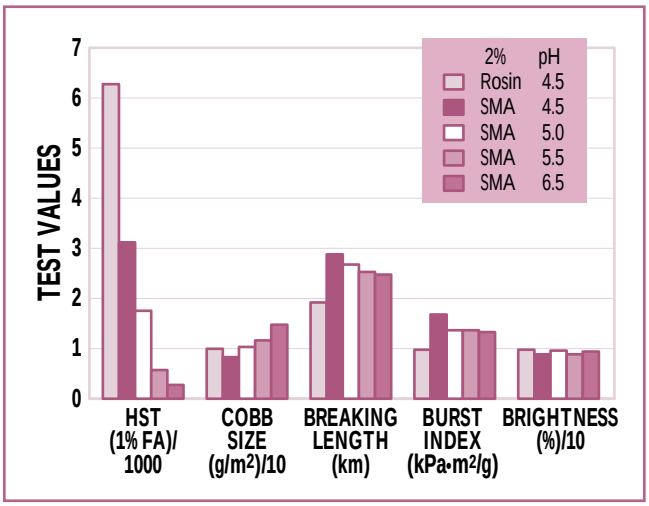
Strength properties

The strength of the sized sheets was tested for the case of unbleached Douglas-fir kraft pulp sized by polymer 1 (2% of dry pulp weight) in solutions of various pH and with different mordants (Figs. 3 and 4). The strength properties for sizing with 2.5% ferrous ion peaked at pH 6.5. For sizing with 2.0% alum, the strength properties peaked at pH 4.5. Rosin sizing showed approximately the same breaking length and burst index regardless of the mordant used. SMA sized unbleached Douglas-fir kraft pulp with ferrous chloride as mordant gave an increase of 59% in breaking length and 65% in burst index compared to rosin. Alum as mordant showed a 49% increase in breaking length and a 51% increase in burst index when compared with rosin sized paper at the same conditions. This large improvement in strength properties warrants further investigation. Due to the darker color imparted by the iron mordant, the use of this type of sizing would be restricted to those products where the brightness and color of the sheet were not important.

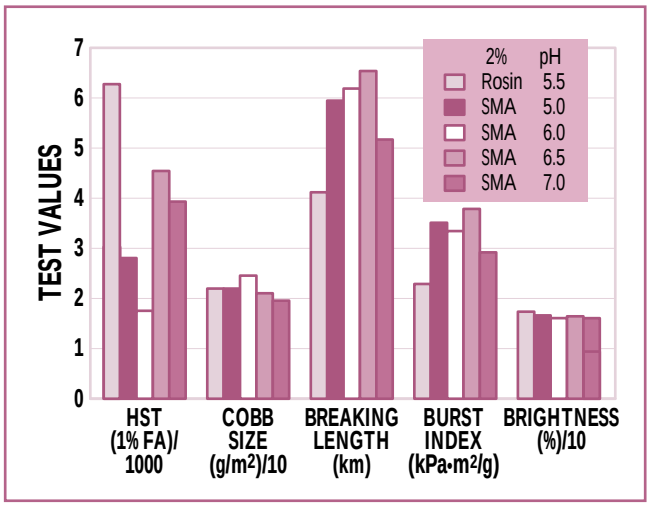
No data were collected measuring the retention of saponified SMA on the pulp fiber in the absence of mordant. However, we do know that no sizing was observed with SMA in the absence of mordant. While some sort of coordination chemistry probably occurred between the polymer and the pulp in the absence of mordant, the negative surface charge carried by both would tend to inhibit any such interaction. Once the mordant was added, the polymer, mordant, and fiber surface interacted to form an insoluble surface layer. Additional changes in precipitate and fiber morphology may have subsequently taken place during drying. The end result was that the fiber surface became more hydrophobic. This water repellency is reflected in the sizing effect.

There are three possible mechanisms of deposition of the sizing agents:

1. The precipitate is formed in solution and then deposited on the pulp fiber surface.
2. The polymer initially adheres to the fiber surface prior to precipitation.
3. The mordant ion binds to the surface and subsequently to the polymer.



3. Sizing and strength properties as a function of pH for unbleached Douglas-fir kraft pulp with alum (2% dry pulp) as mordant and polymer I (2% dry pulp) as sizing agent



4. Sizing and strength properties as a function of pH, unbleached Douglas-fir kraft pulp with ferrous chloride (2.5% dry pulp) as mordant and polymer I (2% dry pulp) as sizing agent

A mixture of these mechanisms may also exist depending upon local concentrations of polymer, ion, fiber surface, pH, and temperature. The actual precipitation step is undoubtedly complicated, but in the case of the SMA copolymers studied here, it probably involves the lignin component of the pulp. This interaction could be between the mordant ion or the SMA backbone and the lignin component, or both. In any case, our results indicate that the sizing effect requires the presence of lignin or other components removed by bleaching. Since this is true for both alum and iron mordants with SMA, and not true for alum and rosin on bleached pulps, some sort of interaction between the polymer backbone and the lignin component is suggested.

Future research will investigate the nature of the polymer-mordant-lignin interaction in greater detail. We will also address the structure-activity relationships between SMA copolymer and the strength of the final sized paper.

CONCLUSIONS

SMA copolymers were effective internal sizing agents for unbleached pulps when used in conjunction with either ferrous chloride or alum mordants. The sizing effect was a complicated function of mordant, copolymer, and lignin interaction. Sizing improved with increasing polymer concentration and was optimized at pHs specific for the mordant.

SMA copolymers were ineffective as sizing agents on bleached pulps using either ferrous chloride or alum as mordants. This result suggests that interaction of polymer or mordant, or both, with the lignin component of the wood fiber (or other components removed by bleaching) was critical for the development of the sizing effect.

The sizing effect appeared to be relatively unaffected by the molecular weight or MA content of the polymer.

The use of an SMA sizing agent on unbleached Douglas-fir kraft pulp improved the strength properties 50–60% compared to rosin sizing. Ferrous chloride as mordant showed slightly greater strength increases compared to alum. However, the brightness of the final sheet was greatly reduced.

The large improvement in strength properties warrants further research into this potentially significant development in sizing.

EXPERIMENTAL PROCEDURE

Materials

The unbleached Douglas-fir kraft pulp had Canadian Standard freeness (CSF) of 450 mL and a Kappa number of 62. It was obtained from the Willamette Industries paper mill in Albany, OR.

The unbleached thermomechanical pulp (TMP) had a Canadian Standard freeness (CSF) of 380 ml. It was obtained from the Smurfit Newsprint Corporation mill at Newburg, OR. The wood species were primarily hemlock and true firs, with a small amount of spruce. The fiber was obtained from the slurry stream prior to bleaching and dried overnight at 60°C. Because it had been oven-dried, this pulp was not used to determine strength properties.

These were the SMA copolymers utilized as sizes:

Polymer 1: Styrene/maleic anhydride copolymer (SMA) with a weight average molecular weight of 50,000 and a MA content of 50%, obtained from Scientific Polymer Products Inc., Ontario, NY.

Mordants	Amount added, % dry pulp	pH	Polymer type*	Amount added, % dry pulp	HST (Neutral)	Cobb Size, g/m^2	Brightness, %
Bleached Hardwood Chemical Pulp							
$FeCl_2$	2.5	5.5	1	2.0	<4	Soaked	50.7
$FeCl_2$	2.0	4.5	1	2.0	<4	Soaked	81.2
$FeCl_2$	2.0	4.5	2	2.5	<4	Soaked	83.8
$FeCl_2$	2.0	4.5	3	2.5	<4	Soaked	85.6
Bleached Douglas-fir Kraft Pulp							
$FeCl_2$	2.5	5.5	1	2.0	8	Soaked	48.3
Alum	2.0	4.5	1	2.0	270	34.6	n/a

*See Experimental Procedure section

III. Bleached pulp sizing with various polymers and mordants

Polymer 2: SMA copolymer with a weight average molecular weight of 1600 and a MA content of 50%, obtained from Scientific Polymer Products Inc., Ontario, NY.

Polymer 3: SMA copolymer with a weight average molecular weight of 1900 and a MA content of 25%, obtained from Polysciences, Inc., Warrington, PA.

The saponified SMA samples were prepared by adding 5g of SMA to 200 mL of a 1% NaOH solution. The slurry was stirred and heated at 80°C for about 12 hours until the solution became transparent, indicating that the polymer had saponified and dissolved. This stock solution was diluted to 0.5% polymer before addition to the pulp slurry.

Alum was obtained from General Chemical, Inc., Parsippany, NJ. Stock solutions of 2% concentration as $Al_2(SO_4)_3 \cdot 14H_2O$ in distilled water were prepared.

Ferrous chloride was obtained from Fisher Scientific as $FeCl_2 \cdot 4H_2O$. Stock solutions of 2% concentration as $FeCl_2$ in distilled water were prepared. These solutions were prepared fresh for each experiment to reduce the oxidation of ferrous ions to ferric. Ferric chloride was insoluble under the conditions of these tests and was observed as a brown colloidal suspension in the solutions.

Pulp slurries

Pulp slurries were prepared by mixing 6 g of pulp (dry basis) in 450 mL tap water. The resulting slurry was blended in a food processor for a few seconds and then stirred for 5–10 min to ensure a well distributed stock. Then the desired amount of 0.5% polymer solution was added and the slurry stirred for 3–5 min. The pH of the slurry was adjusted to the desired value (pH = 6.5 for $FeCl_2$ and pH = 5.5 for alum) using dilute solutions 0.5% to 1% of NaOH and H_2SO_4. The required amount of mordant solution was then added (except as noted). Those samples using ferrous ions as mordant were stabilized at pH = 5.0 for three or more hours, and stock with alum as mordant was stabilized at pH = 4.0 for the same or more time periods before handsheets were made.

The slurry was then diluted to 5.0 L with pH-adjusted tap water. The pH of the slurry was adjusted to the desired value for each trial condition using 1% NaOH and 1% H_2SO_4 solutions. The resulting slurry was mixed thoroughly, and an 800 mL aliquot was removed for each handsheet. This gave a handsheet of approximately 1.2 g. This aliquot was added to the sheet machine cylinder which had been previously filled with approximately 3 L of pH-adjusted water. TAPPI T 205 om-88 was followed to form a handsheet in a British sheet mold. Six handsheets were made for each test. The handsheets were dried in a sheet dryer for 5 min at a temperature of 250°F. They were then moved to a conditioning room maintained at 72°F and 50% relative humidity for at least 24 hours prior to testing.

Handsheets

One handsheet was used for the Cobb size test. Cobb size values were determined by TAPPI T 441 om-90. The remaining handsheets were used for HST and strength tests. Hercules Size Tests were measured according to TAPPI T 530 pm-89 to 80% reflectance values using 1% formic acid solution or neutral ink solution. The test was performed once on each of five handsheets and the results averaged. Typical standard deviations were about 20%. Breaking lengths (tensile breaking strength) were measured according to TAPPI T 404 cm-92 with the Thwing-Albert tensile tester. Two

Amount added, % dry pulp	pH	HST (Neutral)	HST (1% formic acid)	Cobb Size, g/m²	Brightness, %
Alum (2% of dry pulp) as mordant					
0.5	4.5	3,000	830	19.3	18.6
1.0	4.5	3,400	480	32.1	18.0
2.0	4.5	4,000	630	18.0	17.5
2.0 (no mordant)	5.0	n/a	<2	Soaked	17.9
None	4.5	n/a	<2	Soaked	17.8
2.0 (rosin)	4.5	>5,000	1,100	19.3	19.3
$FeCl_2$ (2.5% of dry pulp) as mordant					
0	5.5	n/a	<2	Soaked	17.8
0.5	5.5	>4,500	660	24.5	15.1
2.0	5.5	>4,500	1,970	25.2	15.8
2.0 (rosin)	5.5	>5,000	3,011	21.9	17.0

IV. Effect of polymer 1 concentration on sizing of unbleached Douglas-fir kraft pulp

KEYWORDS

Aluminum sulfate, chlorides, copolymers, ferrous compounds, kraft pulps, lignins, maleic anhydride, mordants, Pseudotsuga, size, styrene, thermomechanical pulps.

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strips were cut from each handsheet, each one measuring 15 mm by approximately 15 cm (7 in.). Ten strips were measured for each trial condition and the results averaged. Typical coefficient of variation values were approximately 5%. The burst index (Mullen testing) was measured according to TAPPI T 403 om-91 with the Model "C" Mullen tester. Each handsheet was tested once, and five handsheets were measured for each trial condition. The results were averaged. Typical coefficient of variation values were found to be about 8%. **TJ**

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