

The Influence of Poly(styrene Sulfonate) Addition to Cellulosic Fibers by Wet Processing on the Physicomechanical Properties of Paper

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Synopsis

The study of the effect of sodium poly(styrene sulfonate) addition to suspensions of fibers, in the presence of aluminum salts as adsorption aids, revealed the retention effect of fine solids during sheet formation. Polyelectrolyte adsorption also causes an increase of bounding energy in the web. It is shown that the improvement observed for the dry strength properties of paper is a consequence of these two effects. (In this paper the words "fine solids" or "fines" indicate the parts of the cellulosic material which filtrates through a 150-mesh screen, regardless of its nature.)

INTRODUCTION

In a previous paper, it was shown that poly(styrene sulfonate) adsorption onto a fibrous network is probably the result of a coflocculation mechanism if aluminum salts are used as adsorption aids.¹ Two operating procedures are possible. The polyelectrolyte can be put into contact with the fibers first, followed by the aluminum salt; this essentially produces polymer precipitation within the suspension. The aluminum salt can also be put into contact with the fibers, and afterward the polyelectrolyte is introduced; the latter interacts with the fiber surface on which metallic ions are adsorbed. In this case, it was shown that the yields of polyelectrolyte adsorption onto cellulosic fibers are good when the polymer weight fraction in relation to the fibers is below or equal to 1% and when the operating conditions are such that the electrokinetic potential of the fiber suspension is close to zero. It had been noted¹ that this second method of polyelectrolyte adsorption onto papermaking fibers could be accompanied by an improvement of some physicomechanical properties and other characteristics of paper. On the other hand, polyelectrolyte precipitation within the fibrous network does not involve any significant improvement.

We have attempted to correlate the effect of polyelectrolyte retention both on fines retention of papermaking pulp and on the fiber-to-fiber bonding power. The variations of these two parameters can indeed account for the observed modifications of properties.

It is known that coflocculation mechanisms involve an increase of the fines retention of fiber suspensions.² Consequently, an increase of retention can be considered as evidence for the occurrence of this mechanism.

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TABLE I
Pulp Characteristics After Various Beating Operations^a

	Standard beating				Beating followed by fines removal		
	0 min	16 min	38 min	43 min	16 min	38 min	43 min
°SR	14	20	46	56	15	20	22
Tappi drainage factor, sec	(a) 5.2	5.5	13.0	19.7	(a') 5.8	6.8	8.4
	(b)	4.9	16.5	20.5	(b') 5.0	7.4	8.8
	(c)	5.7	24.0	31.0	(c') 5.2	6.0	8.3
Fractionating	$R_{28} = 75.6$	66.0	51.8	49.5			
Bauer-McNett apparatus, %	$R_{28/48} = 12.8$	16.2	19.2	10.0			
	$R_{48/65} = 5.5$	7.0	10.5	10.5			
	$R_{65/100} = 2.5$	5.0	7.6	8.6			
	$R_{200} = 3.6$	5.8	10.9	21.4			

^a (a) Blank beating; (b) beating in presence of 5% aluminum chloride; (c) as in (b) +2.5% poly(styrene sulfonate)/pulp; (a') as in (b) with washing before sheet forming; (b') as in (a') +2.5% aluminum chloride; (c') as in (b') +2.5% poly(styrene sulfonate)/pulp.

EXPERIMENTAL

The synthesis of poly(styrene sulfonic acid) has been described in a previous paper.¹

Pulps were refined in a Valley beater and their drainability was measured by determining their drainage factor according to the usual operating method.³ Paper sheets were made on the laboratory sheet-forming machine Frank.

During sheet manufacture, fines retention was directly controlled under the wire during sheet formation on the laboratory machine by retrodiffusion turbidimetric measurements with the apparatus designed by Silvy and Pascal.⁴

Dry solids content of white water, expressed in mg for 2 g of pulp, was calculated by measuring the difference between the weight of the dry residue of water used for sheet manufacture and that of white water. An average number was obtained from three measurements. Experimental details have been described elsewhere.⁵

RESULTS AND DISCUSSION

Study of Pulp Fines Retention

In this section we attempt to emphasize the effect of poly(styrene sulfonate) on fines retention, which can explain the possible improvement of the physical characteristics of the papers obtained thanks to the network reinforcement created by retention.

During a first beating in a Valley beater, a sufficient amount of bleached softwood soda pulp was introduced so that three successive samplings could be made at different beating intervals. Beating was carried out in the presence of 5% aluminum chloride/pulp weight. Blank sheets were then made both in the presence of aluminum chloride alone and with 2.5% poly(styrene sulfonate). A beating without aluminum salt under identical conditions was carried out for comparison.

In the third beating operation, performed under the same conditions as previously described, the pulp samplings were washed on a 150-mesh screen in order

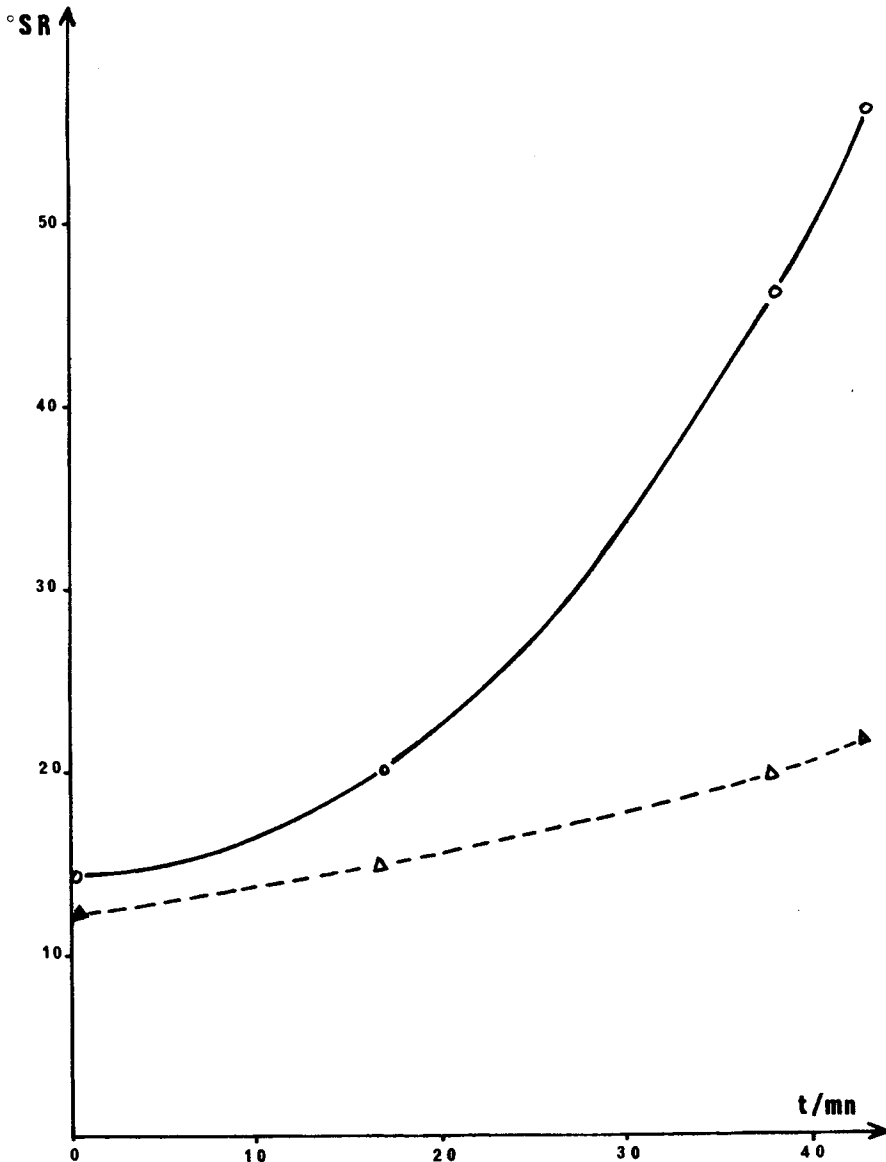


Fig. 1. Drainage factor vs. beating time (bleached softwood soda pulp). Dashed curve for washed pulp on a 150-mesh screen.

to remove fine solids. From these washed samplings, three series of sheets were prepared: the first one from the pulp thus handled; the second with 2.5% aluminum chloride added; the third with 2.5% poly(styrene sulfonate) added, in addition to previous aluminum salt treatment.

The fines retention control was carried out directly under the sheet-forming machine wire with the turbidimetric apparatus. Matter in suspension was determined by dry evaporation on the samplings, taking into account the mineral salt content of the water used. Table I gives the results of drainage measurements and pulp fractionations for this study (Fig. 1) measured as Shopper-Riegler index.

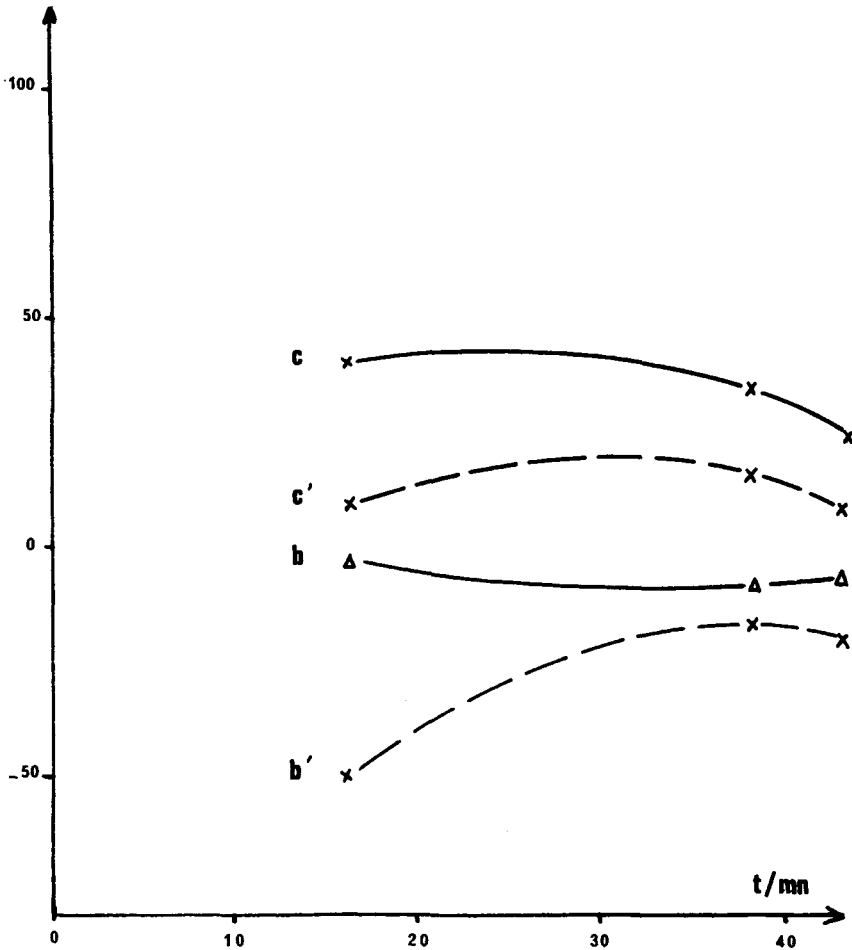


Fig. 2. Breaking strength ratio (%) vs. beating time (bleached softwood soda pulp); (b), (b'), (c) and (c') have the same meaning as in Table I. The ratios have been calculated for (b) and (c) relative to (a), and for (b') and (c') relative to (a'). The dashed curves concern a pulp for which fines have been eliminated by washing: (—) with fines; (- - -) without fines.

Table I shows the effect of beating on fines fraction which steadily increases with beating time. We can also note the influence of these fines on pulp drainage factor, in comparison with the results in the presence of, and without, fines: filtration resistance remains low after 43 min of beating when these fines are removed. Furthermore, the effect of poly(styrene sulfonate) as fines retention aid appears quite clearly when the value of stock drainage, with and without aluminum chloride, is considered [results (a) and (b), as compared to the value of stock drainage factor with polymer, result (c)]. Drainage factors are considerably higher in the presence of polymer, all the more as the stock contains a great amount of fines. The relative variation on the drainage factor is above 50% for beating times of 38 and 43 min.

The study of the variations of paper physicommechanical characteristics as related to beating, to its fines content, aluminum salt, and poly(styrene sulfonate) content was also carried out. All the data are given in Tables II and III.

TABLE II
Evolution of Physical Characteristics as Related to Beating with and without Poly(styrene Sulfonate), with and without Fines^a

	0 min	Standard beating			Beating followed by fines removal		
		16 min	38 min	43 min	16 min	38 min	43 min
°SR	14	20	46	56	15	20	22
Basis weight, g/m ²	(a)	77.1	70.0	70.8	(a')	68.7	70.7
	(b)	—	73.9	70.0	(b')	69.7	69.2
	(c)	—	73.0	70.1	(c')	69.2	67.8
Moisture content, %	(a)	7.2	6.8	6.8	(a')	7.8	8.6
	(b)	—	6.6	6.7	(b')	7.9	8.4
	(c)	—	7.8	8.1	(c')	8.4	8.5
Thickness, μm	150	113	106	107	116	115	106
	(a)	121	107	100	b'	117	102
	(c)	117	104	96	c'	102	100
Specific volume, cm ³ /g	1.95	1.60	1.52	1.51	1.68	1.54	1.50
	(a)	1.64	1.45	1.43	b'	1.70	1.47
	(c)	1.60	1.42	1.37	c'	1.69	1.47
Air permeability AFNOR	53.9	19.2	2.0	1.1	50.2	13.4	8.5
	(a)	22.0	1.3	0.5	a'	76.6	9.0
	(b)	18.9	1.1	0.5	c'	74.7	13.6
Breaking strength, (m) LR	2300	5100	5800	6600	4200	5000	5400
	(a)	5000	5400	6200	b'	2120	4400
	(c)	7100	7900	8200	c'	4600	5850
Elongation, %	2.2	3.0	3.0	3.2	2.6	2.8	2.8
	(a)	2.9	2.9	3.0	b'	1.5	2.6
	(c)	3.8	3.5	3.5	c'	3.0	3.4
Zero span breaking strength, (m) LR ₁	11400	11300	11300	12900	13100	12700	13700
	(a)	14000	13000	13500	b'	10100	12500
	(c)	13200	13100	12800	c'	11800	12300
Bonding factor, LR/LR ₀ × 100	20	42	50	50	32	40	39
	(a)	35	41	40	b'	21	35
	(c)	54	60	64	c'	39	47

^a (a), (b), (c), (a'), (b'), and (c') have the same meaning as in Table I.

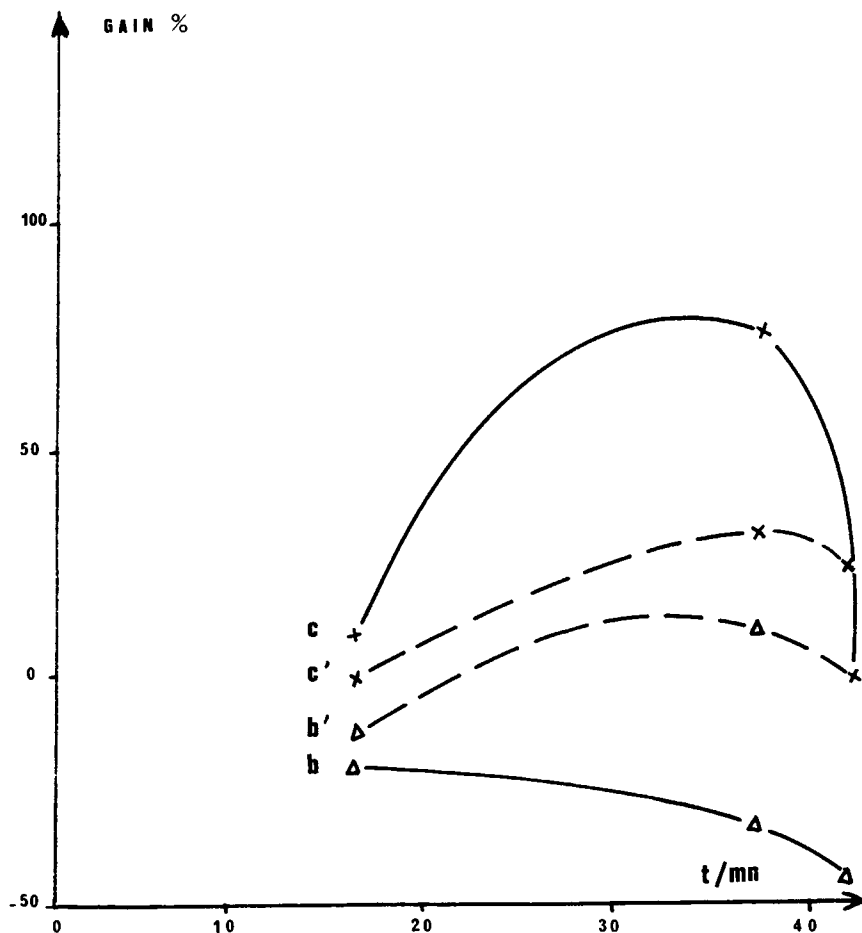


Fig. 3. Dynamic stiffness ratio (%) vs. beating time; (b), (b'), (c), and (c') have the same meaning as in Table I. Same calculations as for Fig. 2 (see Fig. 2 caption): (—) with fines; (- - -) without fines.

It is to be noted that air permeability decreases normally as beating degree increases, but it is higher in the absence of fines with the polymer. The polymer and fines have an outstanding influence on the improvement of mechanical properties such as breaking strength, Young's modulus, breaking strain, dynamical stiffness, bursting factor, internal bonding degree, and cohesion, as shown in Tables II and III and Figures 2-7. At the same time, in the case of sheets made with fines, a decrease of the tearing strength is noted, which seems less important at a high beating level than at short-time beating. Breaking strength variations are of particular interest to enhance the respective role played by fines and by the polymer (Fig. 2). Breaking strength increases by 25-40% in the presence of poly(styrene sulfonate) with fines, whereas it increases only by 10-15% in the presence of this polymer but in the absence of fines (Fig. 2). We can also note a relative increase of the bonding factor, 20-30% with fines and 20% without fines, i.e., new bonds are built in the presence of the polymer (Fig. 7).

On the whole, it is to be noted that the polymer cancels out the harmful effect

TABLE III
Evolution of Mechanical Characteristics as Related to Beating with and without Poly(styrene Sulfonate), with and without Fines^a

	Standard beating			Beating followed by fines removal		
	0 min	16 min	38 min	16 min	38 min	43 min
°SR	14	20	46	56	15	22
Young's modulus <i>E</i> , kg/m ²	(a) 129	(b) 271	(c) 320	(a') 373	(b') 218	(c') 295
Breaking energy, J/g	—	256	306	344	194	268
	—	376	494	583	281	377
	120	372	470	625	368	425
	—	368	425	564	111	401
	—	734	981	1061	378	552
Dynamic stiffness, nN × 10 ⁻³	0.3230	0.29	0.23	0.23	0.28	0.19
Concora medium test, kg/cm ²	—	0.24	0.21	0.17	0.25	0.19
	—	0.32	0.42	0.24	0.28	0.31
	6.2	13.0	16.1	12.1	11.6	13.5
	—	13.6	18.5	16.7	8.6	17.4
	—	17.6	17.7	17.6	14.2	15.3
Bursting factor	1.87	4.2	4.6	4.9	3.0	3.9
K.P.	—	4.3	4.9	4.8	1.2	3.0
	—	6.0	5.6	5.6	3.4	4.6
Tearing factor	2070	1170	1020	970	1530	1090
<i>I</i> ₀ 100	—	1060	920	880	1140	1150
Internal cohesion energy, J/m ²	—	910	850	930	1500	1060
Variation coefficient	(a)		366			378
<i>V</i> , %			<i>V</i> = 5%			<i>V</i> = 7%
	(b)		608			254
	(c)		<i>V</i> = 4%			<i>V</i> = 11%
			717			552
			<i>V</i> = 4%			<i>V</i> = 36%

^a (a), (b), (c), (a'), (b'), and (c') have the same meaning as in Table I.

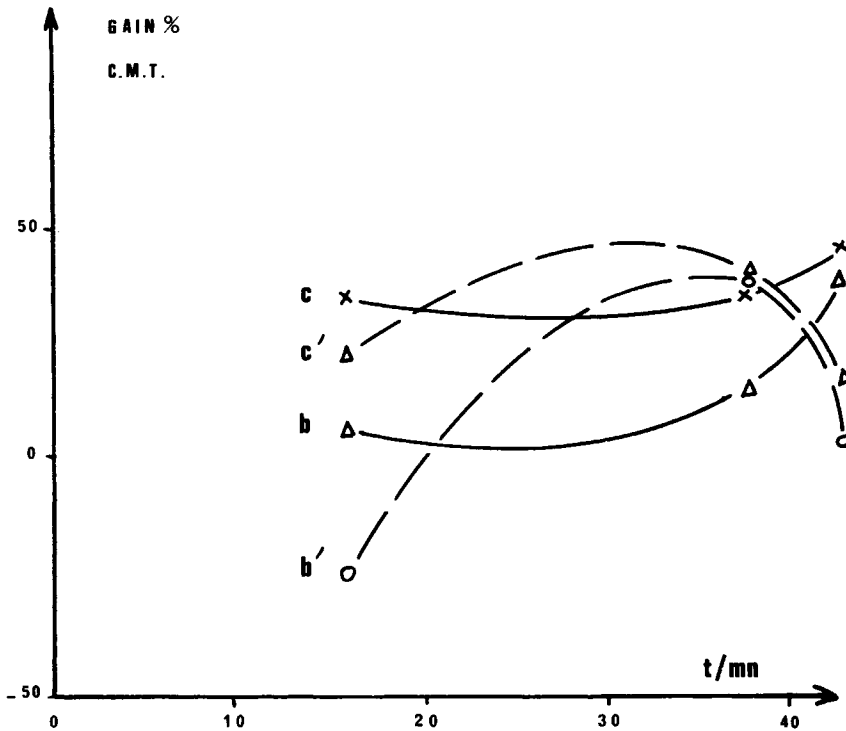


Fig. 4. Stiffness ratio (%) as given by the Concora medium test (C.M.T.) method. Same calculations as for Fig. 2 (see Fig. 2 caption): (—) with fines; (- - -) without fines.

of aluminum salt and there is even a real gain as compared to the blank paper. Breaking strain and internal cohesion are the characteristics which increase most when polymer is added, and the highest gains were observed in the presence of fine solids.

The effect of poly(styrene sulfonate) on paper stiffness is of particular interest. The characteristic improvement could as well be ascribed to the polymer presence as to fines retention, although in other respects a decrease in paper mass volume may be observed. Under the same conditions, paper tearing strength its practically maintained.

Table IV shows the evolution of the optical properties of papers obtained in the same series of tests. Brightness and opacity variations are low. A slight (0.8) brightness gain can be noted under the effect of aluminum chloride addition followed by that of poly(styrene sulfonate) in the presence of pulp fines. Brightness, on the other hand, decreases by 1.2 points under identical conditions when there are no fines.

These results can be explained by the coupled action of increase of whiteness effect due to aluminum chloride and by an increase in absorption characteristic of the polymer. It is to be noted, indeed, that the mass absorption coefficient K' of tests (b) in the presence of aluminum chloride is systematically lower than that of tests (a), where aluminum ion is absent. On the contrary, the mass absorption coefficient value increases every time polymer is added whether in the presence or in the absence of fines. Paper mass diffusion coefficient values S' when they decrease characterize an increase in fiber-to-fiber or interfiber

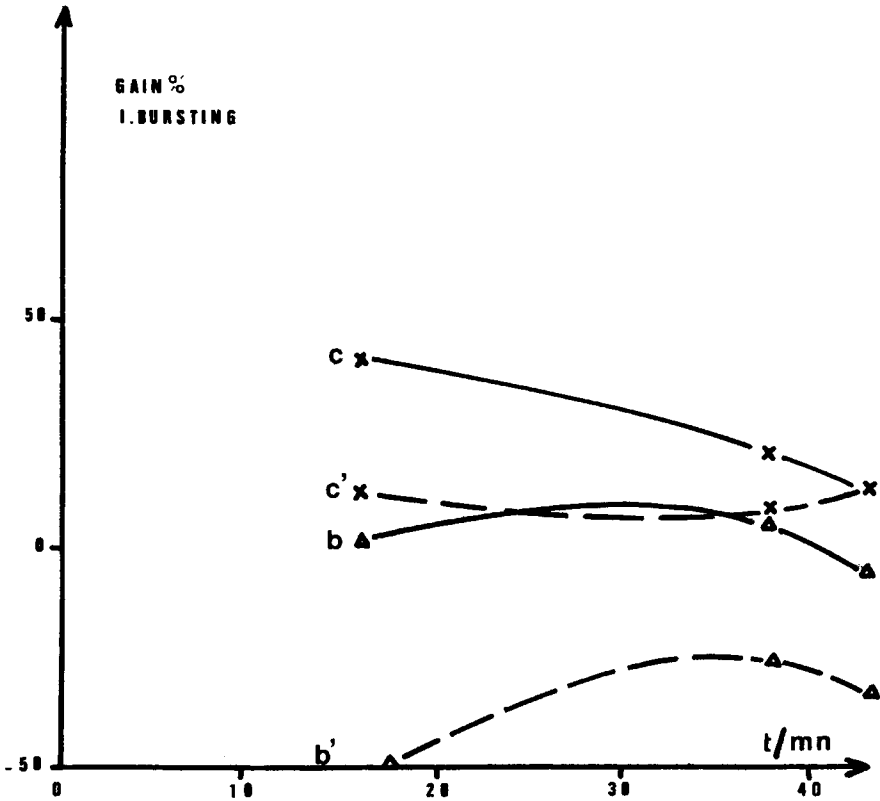


Fig. 5. Bursting Index ratio (%) vs. beating time. Same calculations as for Fig. 2 (see Fig. 2 caption): (—) with fines; (- - -) without fines.

bonding. It is in this way that we can explain breaking strength and internal cohesion values which are at their highest level in the presence of fines and of the polymer, tests (c), as well as the polymer positive effect on interfiber bonding, judging by the results of tests (c') and (b').

In the same series of tests we have attempted to measure the influence of sodium poly(styrene sulfonate) on fines retention (Table V). The turbidity of white water notably decreases under polymer action, considering that the fines portion in the pulp is important. The dry extract of white water corroborates the high efficiency of poly(styrene sulfonate) as fines retention aid. The presence of aluminum salt increases the weight amount of solids dissolved in white water, as shown by the comparison of the results (a) and (b), but its action as fines retention aid in the pulp causes a decrease of turbidity and of suspended solids content of white water, especially when fines are present in the pulp.

The ash content has been calculated according to NFQ 03-047. Poly(styrene sulfonate) decomposition and combustion is completely achieved under the conditions of paper incineration. That is why this factor is hardly sensitive to the presence of the polymer.

What can the improvement of mechanical properties, which has been observed several times, be ascribed to? It seems that one of the major factors is precisely the fines retention that has been noted. This is accounted for by the fact that we have noted particular improvement for the most refined pulps, i.e., those

TABLE V
Poly(styrene Sulfonate) Effect on Pulp Fines Retention^a

	Standard beating			Beating followed by fines removal		
	0 min	16 min	38 min	16 min	38 min	43 min
°SR	14	20	46	15	20	22
Turbidity of white water	6.1 ± 0.3	5.7 ± 0.4	9.8 ± 0.7	2.2 ± 0.3	2.9 ± 0.2	3.0 ± 0.3
arbit. unit	—	4.0 ± 0.3	7.1 ± 0.3	2.6 ± 0.15	3.0 ± 0.2	3.9 ± 0.16
Dissolved and suspended solids, ^b mg/g	150	140	140	2.0 ± 0.1	1.8 ± 0.2	2.3 ± 0.9
	—	185	375	88	150	175
	—	0.00	0.00	39	150	350
	—	0.00	0.00	0.00	0.00	0.00
Paper ash content, %	0.18	0.18	0.19	1.32	1.47	1.41
	—	1.93	1.93	2.25	2.45	2.51
	—	1.88	1.88	2.20	2.46	2.49

^a (a) Blank beating; (b) beating in presence of 5% aluminum chloride; (c) as for (b) + 2.5% poly(styrene sulfonate)/pulp; (a') as for (b) followed by washing pulp before sheet forming; (b') as for (a') + 2.5% AlCl₃; (c') as for (b') + 2.5% poly(styrene sulfonate)/pulp.

^b Dry extract corrected from mineral salts present in the water used.

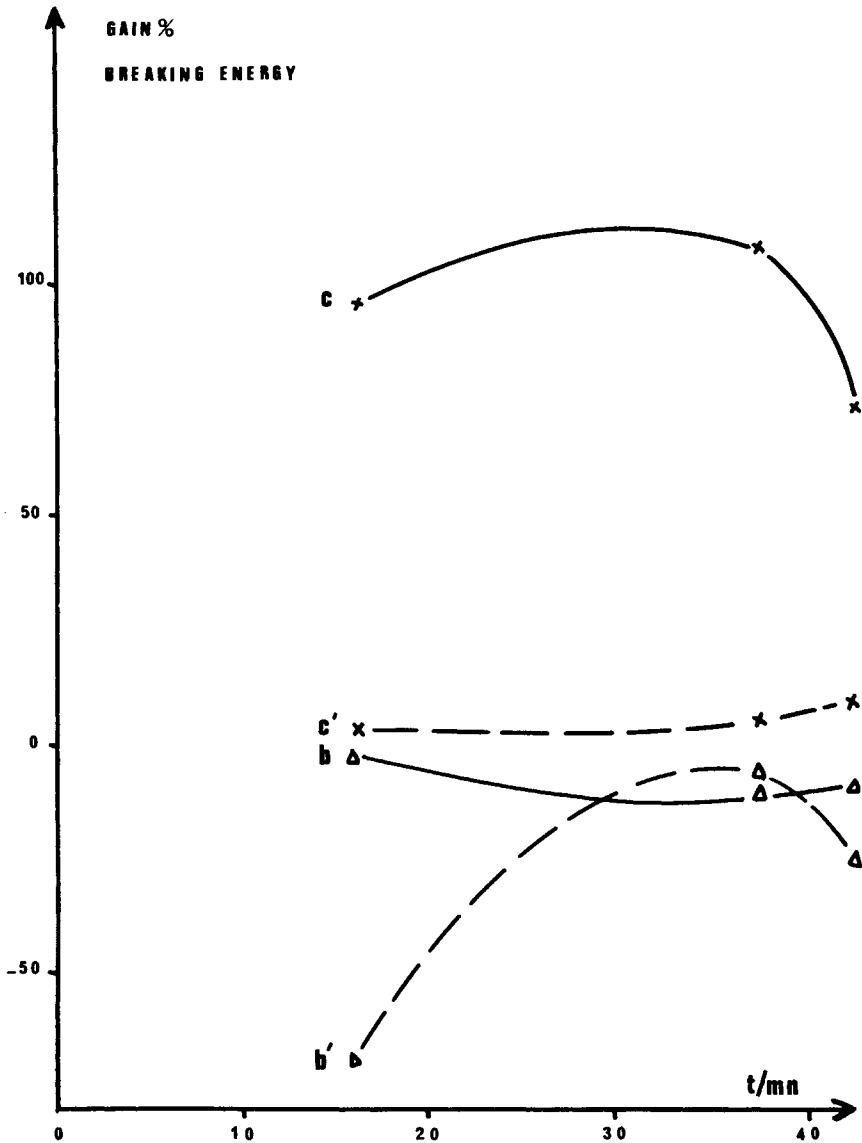


Fig. 6. Breaking energy ratio (%) vs. beating time. Same calculations as for Fig. 2 (see Fig. 2 caption): (—) with fines; (---) without fines.

which contain the highest proportion of fines. We may ask the question: Does the polymer act in any other way apart from fines retention? An examination of our results allows us to conclude in favor of a positive action with respect to interfiber bonding. The polymer leads to an increase of paper internal cohesion which can be noticed even in the absence of fines in the stock. As was already noted under identical conditions, the decrease in the coefficient of paper light mass diffusion was indeed correlated to the increase of sheet interfiber bonding degree. However, the essential part played by aluminum ion on paper mechanical characteristics is also to be stressed. In numerous cases, except for its efficiency as fines retention aid, aluminum ion has reduced the polymer favorable

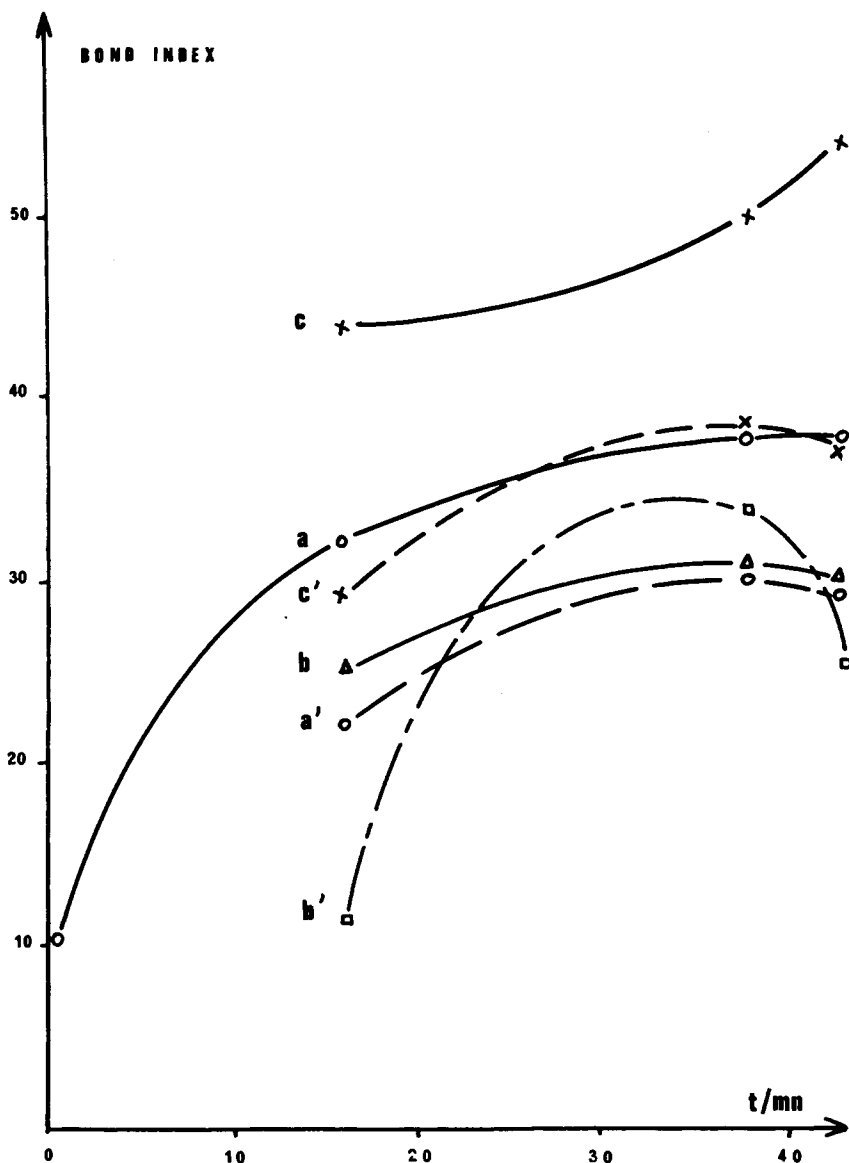


Fig. 7. Bonding factor, $(LR/LR_0) \times 100$, vs. beating time; (a), (b), (c), (a'), (b'), and (c') have the same meaning as in Table I: (—) with fines; (---) without fines.

effects, which hides the gains obtained. This should in fact be considered more important.

CONCLUSION

Poly(styrene sulfonate) is a polyelectrolyte widely used in cation exchange systems. It easily adsorbs aluminum cations dissolved in water. Inversely, if aluminum cations are adsorbed to the cellulose fiber surface and if poly(styrene sulfonate) is dissolved in water, an adsorption of the polymer onto fibers occurs in such a way that during sheet forming ionic interactions lead to an important

increase of the retention of fines, the pulp fine fibrils, as well as to a total increase in bonding power. As a consequence of these modifications, an increase in some mechanical characteristics of paper in the dry state takes place, as has already been observed with other hydrophilic polymers. Important gains are obtained for essential paper properties such as elasticity modulus, stiffness, and internal cohesion power.

It is a well-known fact that a three-component system—cellulose fibers, adsorption aid, polyelectrolyte—is more difficult to control than a two-component system. However, the correlation we have found between good retention of pulp fines and good adsorption of poly(styrene sulfonate), under conditions such that the system electrokinetic potential is close to zero,¹ seems to be logical, a result which is corroborated by research work carried out by other scientists, especially by Strazdins.⁶⁻⁸

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Received November 7, 1979