POLYMERIC ADDITIVE PERFORMANCE IN CLOSED WHITEWATER SYSTEMS

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ABSTRACT

With more stringent requirements on discharge water quality and with escalating water treatment costs, water recycling within the papermill is of growing importance. A serious problem resulting from more whitewater recycling is reduced drainage and fiber or fines retention because of diminished polymeric additive performance.

To provide better insight for overcoming polymeric additive performance problems, this work investigated interactions between pulp furnish and dissolved and/or suspended materials accumulating in whitewater systems. Effects of differing levels of materials carried over from mechanical (water soluble extractives), semichemical (neutral sulfite spent liquor), and chemical (kraft black liquor) pulping were determined with a cationic polyacrylamide and a polyethyleneimine. A drainage testing procedure was used, simulating dewatering processes on the paper machine, measuring drainage rate, fines retention and web dryness in response to vacuum.

Results quantitatively show materials carried over from pulping processes reduce polymer effectiveness as a drainage and retention aid. With increasing levels of carryover, more polymer is required. Carryover affects polymeric additive performance similarly with both dried and never-dried pulp furnishes. The adverse effect of the additive on the web dryness in response to vacuum and on formation was decreased by carryover material.

INTRODUCTION

As quality standards for discharge water have become more stringent, the costs for treating process water have escalated. Primary and secondary treatment systems are already used, with costly tertiary treatment oftentimes needed to meet today's pollution load requirements. The pulp and paper industry, which uses large volumes of process water, has moved to minimize water cleanup costs by reducing the amount of process water discharged, through increased water recycle. Accompanying the increased process water recycle has been a buildup of suspended and dissolved materials, as well as higher water temperatures (1). This buildup is suspected to be the cause of numerous process problems (2, 3). Among

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those are reduced polymeric effectiveness, corrosion, and odor. The severity of these problems varies considerably among mills depending on level of closure, and the extent to which dissolved and suspended materials from one process step are carried into the next. One significant source of such material is from pulping. Pulping liquors can carryover with the fiber furnish into papermaking (3, 4).

With whitewater reuse on the paper machine, reduced effectiveness or ineffectiveness of polymeric additives used to improve drainage rate and fines retention during web formation is also a serious process problem. Polymeric additives are important in furnishes having high fines contents such as recycled, hardwood fiber and high yield pulp. Some work has been done on defining the problems encountered with whitewater closure (3, 5–17). Very limited information, however, is currently available on comprehensively quantifying the effects and sources of dissolved and/or suspended materials on the papermaking process.

In this work, I 1) quantify the effects of differing levels and types of pulping carryover on the effectiveness of a cationic polyacrylamide (PAM) and a polyethyleneimine (PEI) polymeric additive, and 2) determine whether never-dried fiber versus dried fiber furnish influences polymeric additive/pulping carryover interactions.

Materials used as pulping carryover were kraft black liquor, neutral sulfite semichemical (NSSC) spent liquor, and stone groundwood (SGW) extractives. These were never-dried and were used with their respective dried and never-dried fiber furnishes to cover the range of pulping yield. The effects of pulping carryover on polymeric additive performance are measured in terms of pulp slurry drainage and fines retention during web formation, web vacuum dewatering response, wet press dewatering, and web formation as reflected by sheet burst index. With this information, one has increased knowledge of the sources of interfering materials and their effect on the papermaking process. In this way, routes to overcome polymeric additive performance problems can be developed.

RESULTS AND DISCUSSION

Effect of Carryover on PAM

Drainage/Retention. Pulping carryover reduced the effectiveness of PAM as a drainage and fines retention aid when using dried fiber furnishes. This was noted with all three different pulping carryover types and their respective fiber furnishes--kraft black liquor/dried kraft fiber, NSSC spent liquor/dried NSSC fiber, and SGW extractives/dried SGW fiber. However, actual drainage rate and fines retention values varied with the type of fiber furnish (Table I). For example, measured drainage rates with the SGW furnish were lowest due to its high fines content compared to the NSSC and kraft furnishes.

At a given polymeric additive level, drainage rate and fines retention level decreased as pulping carryover level increased (Figs. 1, 2, Table I). Also, as the level of pulping carryover increases, more polymeric additive is needed to maintain drainage and fines retention levels. In Figure 1, for example, with 1% kraft black liquor carryover, 3.5% PAM is required to attain the same drainage rate as that noted with 1% PAM and no black liquor carryover. The pulping carryover apparently acts as a scavenger for the polymeric additive. Using higher levels of

Table 1.--Effect of pulping carryover on 2.5% PAM[1] polymeric additive performance using dried fiber (273 g/m^2 sheets)

Carry-over (weight)	Drainage rate	Fines retention	Solids content after vacuum dewatering	Solids content after pressing	Burst index
%	cm^3/s	%	%	%	$kPa\ m^2/g$
			BLACK LIQUOR/KRAFT FIBER		
0	276	81	--	34.5	3.11
1	178	78	14.4	34.9	3.97
3	136	76	16.0	35.7	3.89
10	133	69	15.3	34.8	4.14
			SPENT LIQUOR/NSSC FIBER		
0	418	--	12.7	40.9	1.57
1	387	84	13.2	40.4	1.67
3	160	83	15.5	40.8	2.78
10	138	74	16.3	40.4	2.83
			EXTRACTIVES/SGW FIBER		
0	51	94	15.6	39.3	1.05
1	61	93	18.4	39.4	1.00
3	37	91	18.2	39.2	0.95
10	28	87	19.6	40.0	0.97
			CONTROL 0% PAM/0% CARRYOVER		
Kraft fiber	160	59	16.3	36.3	4.04
NSSC fiber	138	72	16.9	41.7	2.68
SGW fiber	18	85	19.2	39.5	0.98

[1] (g. PAM/g. ovendry fiber) x 100%.

PAM, however, may not be a practical solution for overcoming the effects of pulping carryover because of economic considerations. At higher pulping carryover levels, such as 10%, greater than 5% polymeric additive is needed to overcome the effects of the kraft black liquor (Fig. 1).

Vacuum Dewatering.--Pulping carryover, in reducing the effectiveness of the PAM as a drainage aid, actually improved web dewatering response to vacuum. Web solids content, in response to vacuum, correlated closely to drainage rate (Fig. 3). The general data trend showed web dryness to decrease as drainage rate increased. The data points in Figure 3 represent varying combinations of pulping carryover and polymeric additive. Webs from SGW, having the lowest drainage rates, attained the highest solids contents (Table I and Fig. 3). Webs from NSSC and kraft fiber, having the highest drainage rates, had the lowest solids contents.

While drainage on the wire improves with polymeric additive, web vacuum dewatering response decreases so the web leaving the wire can have a lower solids content. This can result in lower wet web strength, and can cause problems, particularly with hardwoods and recycled furnishes. The polymeric additive, by flocculating fines and fiber, could produce a web with large pores (18). These pores would allow air to pass more easily, reducing the effectiveness of the vacuum. Another cause for lower web solids content could be the fiber/fines flocs retain water better.

Wet Pressing.--Pulping carryover level, polymeric additive level, and drainage rate had little effect on web solids content after wet pressing. The differences in web moisture contents after vacuum dewatering are eliminated in wet pressing (Table I). These wet pressings were done under static conditions. Under dynamic pressing conditions where nip residence times are much shorter (5-10 ms) than those used here (10 s), differences in web moisture contents noted after vacuum dewatering may persist. If a web has large pores, pressing may move water from the more dense fiber/fines floc regions to less fiber-dense pore regions (19, 20).

Formation.--With increasing amounts of pulping carryover, web formation improved, as monitored by sheet burst index, with the dried kraft and NSSC furnishes (Table I). With SGW, where fines level is high and drainage rates are low, drainage rate had little effect on burst index and formation. The data in Figure 4 represent varying combinations of pulping carryover and polymeric additive levels.

Effect of Carryover Type

Kraft black liquor was the most detrimental to PAM effectiveness as a drainage and fines retention aid when using a fiber furnish mixture--one-third kraft, one-third NSSC, and one-third SGW dried fiber. NSSC spent liquor was the next, followed by SGW extractives. Thus, more polymeric additive is required to overcome the effect of kraft black liquor than NSSC spent liquor or extractives. In Figure 5 for example, with 1% carryover, 4% PAM is needed with the kraft black liquor carryover while 2.7% PAM is needed with NSSC spent liquor and 2.1% PAM with extractives to attain the same drainage rate. At 10% pulping carryover level, little difference in drainage rate and fines retention was measured among the carryover types (Table II). This is probably due to

Table 11.--Effect of pulping carryover on 2.5% PAM[1] polymeric additive performance using a dried fiber furnish of kraft/NSSC/SGW fiber (273 g/m^2 sheets)

Carry-over type	Drainage rate	Fines retention	Solids content after vacuum dewatering	Solids content after pressing	Burst index
%	cm^3/s	%	%	%	kPa m^2/g
		0% CARRYOVER[2]			
--	202	88	16.1	37.2	1.67
		1% CARRYOVER[2]			
Kraft	85	85	18.4	39.4	1.72
NSSC	109	91	17.2	37.0	1.92
SGW extractives	141	88	16.9	37.8	1.80
		3% CARRYOVER[2]			
Kraft	46	82	16.8	36.6	2.18
NSSC	68	84	17.8	37.4	1.99
SGW extractives	77	84	18.6	38.6	1.94
		10% CARRY OVER[2]			
Kraft	53	80	17.7	37.4	1.82
NSSC	47	81	18.0	37.1	2.16
SGW extractives	64	81	18.0	37.1	2.16
		CONTROL 0% CARRYOVER[2]/0% PAM			
--	50	79	18.5	38.7	2.07

[1] (g. PAM/g. ovendry fiber) x 100%.
[2] (g. carryover/g. ovendry fiber) x 100%.

having the carryover level high enough to render even the highest level of PAM ineffective.

Carryover type had little, if any, effect on web solids content after wet pressing (Table 11). Vacuum dewatering and formation (Fig. 4), again correlate with drainage rate, so carryover type has an effect. The higher the drainage rate the lower the web solids content after vacuum dewatering and the poorer the formation. Because kraft black liquor has the greatest effect on reducing polymeric additive effectiveness as a drainage aid, it also has the largest effect on improving vacuum dewatering and formation.

While this investigation used never-dried carryover with dried fiber, it remains to be shown that dried carryover acts the same as never-dried carryover. This is an important point to demonstrate for mills using recycled fiber and market pulp.

Effect of Carryover on PEI

The overall effects of pulping carryover level and type was similar for PEI (Table III) to that for PAM (Table I). A direct comparison of the two polymers cannot be made because they are used under different pH conditions. As in the case for PAM, PEI effectiveness as a drainage and fines retention aid is reduced as carryover level increased. All three furnish types with their respective carryover types gave similar response as with PAM. However, actual drainage rate and fines retention values varied with type of fiber furnish. At any given PEI level, drainage rate and fines retention level decreased as pulping carryover increased (Table III). As the level of pulping carryover is increased, more PEI is needed to maintain a constant drainage rate level. In Figure 6, for example, with 1% NSSC spent liquor carryover, 1.35% PEI is required to attain the same drainage rate as 0.5% PEI with no carryover. Vacuum dewatering response and formation, as reflected in burst index, also gave the same correlation with drainage rate as PAM (Figs. 3 and 4).

Difference Between Dried and Never-Dried Fiber Furnish

The overall effects of pulping carryover level and type on PAM effectiveness was the same with never-dried fiber (Table IV) and dried fiber furnishes (Table I). However, the measured drainage rates, fines retention levels, vacuum dewatering response, and burst index values differed. In Figure 7, for example, PAM effectiveness as a drainage aid decreases as carryover level increases with both never-dried and dried fiber furnish. The measured drainage rates with the dried fiber furnish are generally higher than with never-dried fiber furnish at any given PAM and carryover level. The general data trends of drainage rate with PAM and carryover are similar, however. This is also evident with vacuum dewatering response as shown in Figure 3. The solids contents in response to vacuum of both the webs from dried and never-dried furnishes decrease as drainage rate increases. The webs from never-dried furnish are approximately 2 percentage points lower in solids content than from dried furnish at any given drainage rate. These differences are attributable to never-dried fiber being more swollen and holding water better than once-dried fiber. Also, once-dried fibers do not bond as well. Therefore, the never-dried fiber furnishes generally had slower drainage rates and lower solids contents in response to vacuum while burst indices are higher than with dried fiber furnish.

Table III.--Effect of pulping carryover on 1.5%[1] PEI polymeric additive performance using dried fiber (273 g/m^2 sheets)

Carry-over (weight)	Drainage rate	Fines retention	Solids content after vacuum dewatering	Solids content after pressing	Burst index
%	cm^3/s	%	%	%	kPa m^2/g
		BLACK LIQUOR/KRAFT FIBER			
0	234	83	14.0	34.1	3.81
1	118	80	15.5	34.7	4.57
3	122	73	--	35.4	4.42
10	--	65	15.8	34.8	4.17
		SPENT LIQUOR/NSSC FIBER			
0	375	84	13.4	32.9	1.94
1	294	84	14.0	34.2	2.05
3	155	80	16.5	34.8	2.45
10	143	73	17.3	35.2	2.45
		EXTRACTIVES/SGW FIBER			
0	85	--	--	--	--
1	67	86	19.4	37.1	0.98
3	33	83	18.6	37.3	0.88
10	22	83	18.2	37.2	0.99

[1](g. PEI/g. ovendry fiber) x 100%.

CONCLUSIONS

Never-dried pulping carryover from kraft, NSSC, and SGW pulping reduced the effectiveness of polymeric additives (PAM and PEI) used as drainage and retention aids. At a given polymeric additive level, as pulping carryover increased, drainage rate and fines retention level decreased until the polymeric additive became completely ineffective. Polymeric additive performance can be maintained by adding increased amounts of polymer, but costs for polymer may become prohibitive. Pulping carry-over, by reducing the effectiveness of PAM and PEI as a drainage aid, improved web vacuum dewatering response and formation.

The never-dried pulping carryover type having the most deleterious effect on PAM effectiveness was kraft black liquor, followed by NSSC spent liquor and SGW extractives.

Table IV.--Effect of pulping carryover on 2.5%[1] PAM polymeric additive performance using never-dried fiber (273 g/m^2 sheets)

Carry-over (weight)	Drainage rate	Fines retention	Solids content after vacuum dewatering	Solids content after pressing	Burst index
%	cm^3/s	%	%	%	kPa m^2/g
			BLACK LIQUOR/KRAFT FIBER		
0	192	92	13.0	32.1	4.22
1	99	88	14.6	32.1	4.77
3	117	75	14.3	32.3	4.98
10	106	69	14.2	32.1	5.05
			SPENT LIQUOR/NSSC FIBER		
a	329	85	12.8	34.4	2.35
1	158	82	13.0	34.0	2.93
3	116	81	14.4	33.8	3.43
10	104	83	14.9	33.7	3.46
			EXTRACTIVES/SGW FIBER		
0	55	91	15.6	35.0	1.06
1	49	91	15.6	35.3	1.00
3	29	89	17.8	35.9	0.89
10	24	87	17.1	34.5	1.13
			CONTROL 0% PAM/0% CARRYOVER		
Kraft fiber	110	80	14.5	31.8	5.82
NSSC fiber	108	70	14.8	33.7	3.11
SEW fiber	23	87	18.2	38.7	1.10

[1](g. PAM/g. ovendry fiber) x 100%.

The overall effects of pulping carryover level and type were the same on PAM when using both dried and never-dried fiber furnishes.

EXPERIMENTAL

Furnishes

Pulps.--Three pulps were used: kraft (51% yield) from loblolly pine (*Pinus taeda* L.), NSSC (75% yield) from 50% red oak (*Quercus falcata*

Michx) and 50% birch (Betula papyrifa), and SGW (~94% yield) from spruce (Picea mariana (Mill.) B.S.P.). All pulps were produced at the U.S. Forest Products Laboratory (FPL). The kraft and NSSC pulps were cooked in a 0.4 m^3 rotating digester. The SGW was produced using a 1.5-m-dia. stone at a peripheral speed of 34 m/s to a Canadian standard freeness (CSF) of 135 ml. The kraft pulp was refined to 630 ml CSF using a 300-mm-dia. single rotating disk pump through refiner at 2.8% consistency. The NSSC pulped chips were refined to 510 ml CSF using a 914-mm-dia. double rotating disk refiner. All pulps were washed on a pulp washer and dewatered.

The three pulps were run separately on the FPL paper machine (0.25% consistency, 6.1 m/min) to produce webs of 205 g/m^2, 127 g/m^2, and 65 g/m^2 from the kraft, NSSC, and SGW pulps, respectively. Never-dried fiber for experimentation was taken as wet lap after the first wet press. Dried fiber was obtained at the reel after drying in the dryer section (177°C).

Wet lap and dried sheets were dispersed in distilled water using a British disintegrator. The NSSC and SGW fiber furnishes were used without further processing. However, the kraft furnishes (never-dried and dried) were reduced to 520 ml CSF in a Valley beater. The fines contents of all the fiber furnishes--including a mixture of all three types--were measured as in Tappi Standard T 261-pin-79 using the equivalent of a 200-mesh screen. Fines contents are:

Fiber Furnish	Fines Content, %	
	Never-dried	Dried
Kraft	8.3	6.2
NSSC	16.2	15.9
SGW	25.8	25.1
1/3 kraft/1/3 NSSC/1/3 SGW	--	19.4

Polymeric Additives.--Two polymeric additives representing differing types in general use were used. One additive was a cationic, high molecular weight, low charge density polyacrylamide (PAM). This additive was used at a pH of 5.5. The other additive was a cationic, low molecular weight, high charge density polyethyleneimine (PEI). This additive was used in the pH range 8.5-9.2. Each additive was used in a pH range in which it was experimentally found to be most effective as a drainage/retention aid. PEI was added over the range of 0-3% based on fiber weight, while PAM was added over the range of 0-5%.

Pulping Carryover.--Pulping carryover material used in drainage/retention measurements was obtained by collecting samples of kraft black liquor and NSSC spent liquor. The samples were collected at the time of blowdown when preparing the kraft loblolly pine and NSSC red oak/birch pulps. Water soluble extractives from spruce were obtained by heating submerged spruce chips in a 0.023 m^3 digester maintained at

100°C for 3 hours. The extractives were concentrated by vacuum boiling at ~40°C.

Solids contents of the pulping liquors were measured as in Tappi Standard T-650. Solids contents were 17.2% for kraft black liquor, 10.8% for NSSC spent liquor and 27.9% for water-soluble spruce extractives. Pulping carryover levels of 1, 3, and 10% solids based on fiber weight were used.

Drainage/Retention Measurements

A modified Britt Water Release Analyzer (21) was used for drainage/retention determinations. The modification made the formed web the principal resistance to flow (18).

The step-by-step procedure is as follows: 1) Fill the jar to the wire with water; 2) add the furnish at the desired consistency; 3) stir the furnish at 5 revolutions per second (rps) while adding the desired level of carryover; 4) adjust the pH to the desired level; 5) stir at 26.7 rps for 1 min to ensure good dispersion; 6) reduce stirrer speed to 5 rps for 2 min; 7) add the polymeric additive (if one is used) and stir for 20 s; 8) open the ball valve to drain the jar, stirrer stops and timer starts (vacuum level 4.22 kPa). The timer automatically shuts off when the liquid level drops below the level-sensing electrodes; 9) increase vacuum level (33.8 kPa) for 6 s; 10) remove the fiber pad, weigh, press between blotters at 690 kPa for 10 s in a flat press, weigh, dry under x-y restraint in a flat press maintained at 177°C, weigh dried sheet; 11) filter filtrate through filter paper and determine fines retention; and 12) calculate drainage rate from the measured drainage time and volume change from starting level to the bottom of the level-sensing electrodes.

Parameters selected to approximate conditions on a paper machine are: grammage--273 g/m^2, consistency--0.23%, polymeric additive/fiber furnish contact time--30 s, shear level as determined by stirrer speed--5 rps, vacuum level during web formation(foils, vacuum boxes, table rolls)--4.22 kPa, and vacuum level after web formation (couch roll)--33.8 kPa.

Property Measurements

Bursting strength of the dried sheet was measured as an indicator of formation. Burst index was measured as in Tappi Standard T-403.

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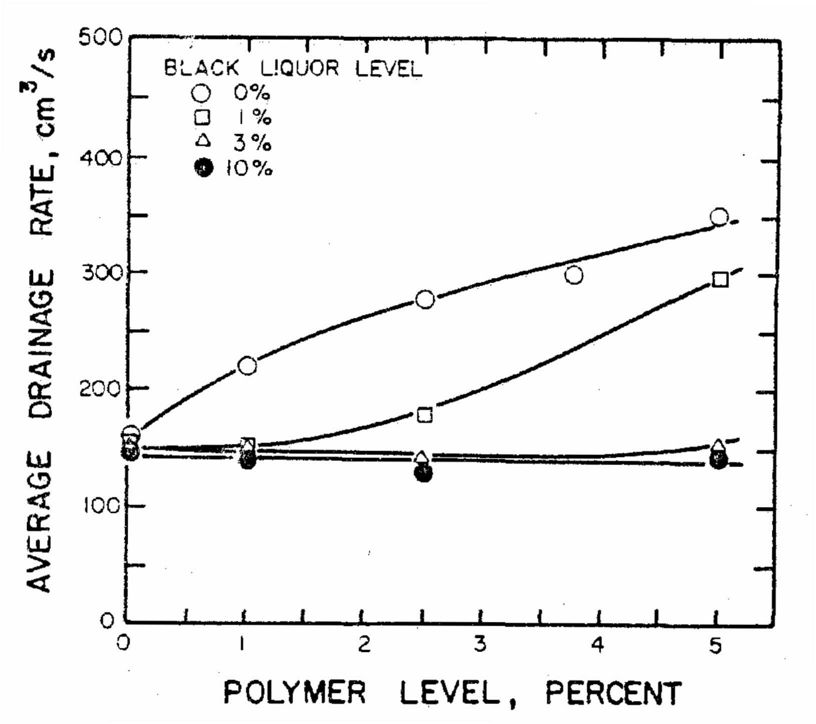

Figure 1. Effect of kraft black liquor pulping carryover on polymer additive (PAM) performance using dried kraft paper.

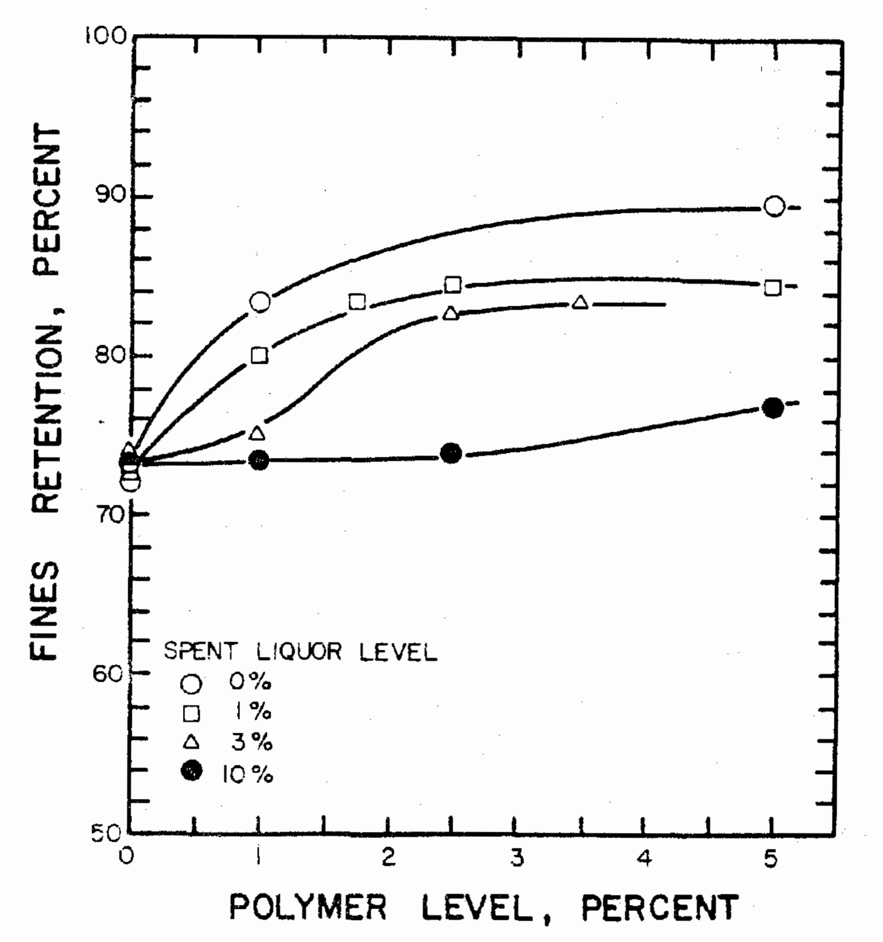

Figure 2. Effect of NSSC spent liquor pulping carryover on polymeric additive (PAM) performance using dried NSSC fiber.

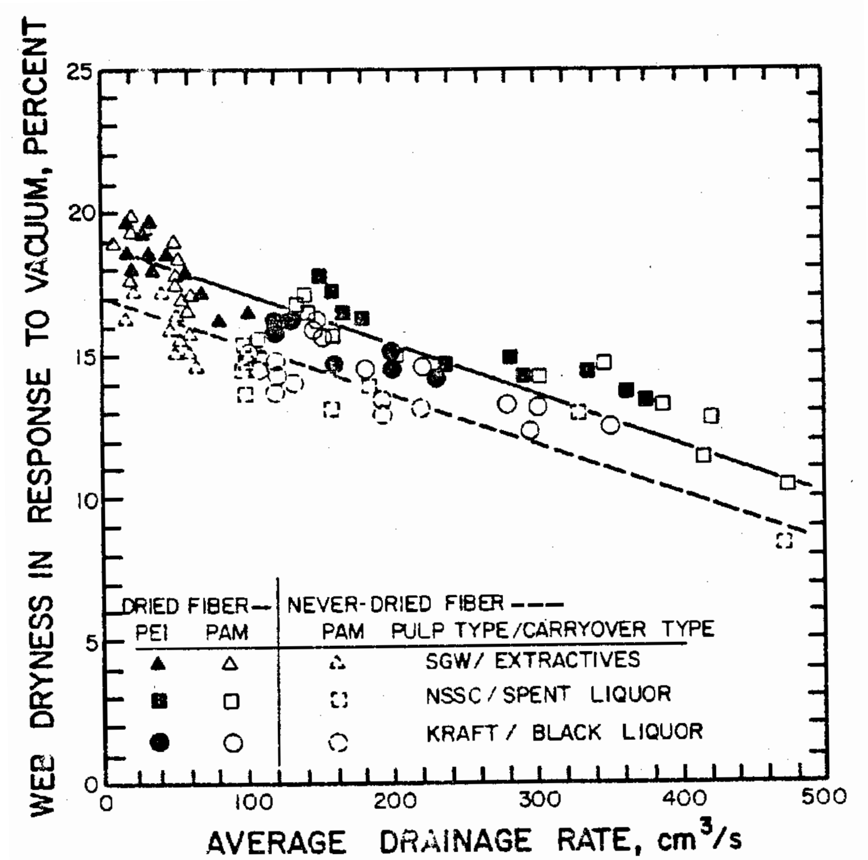

Figure 3. Correlation of drainage rate on web vacuum dewatering response for 273 g/m² webs at varying combinations of polymeric additive and pulping carryover levels.

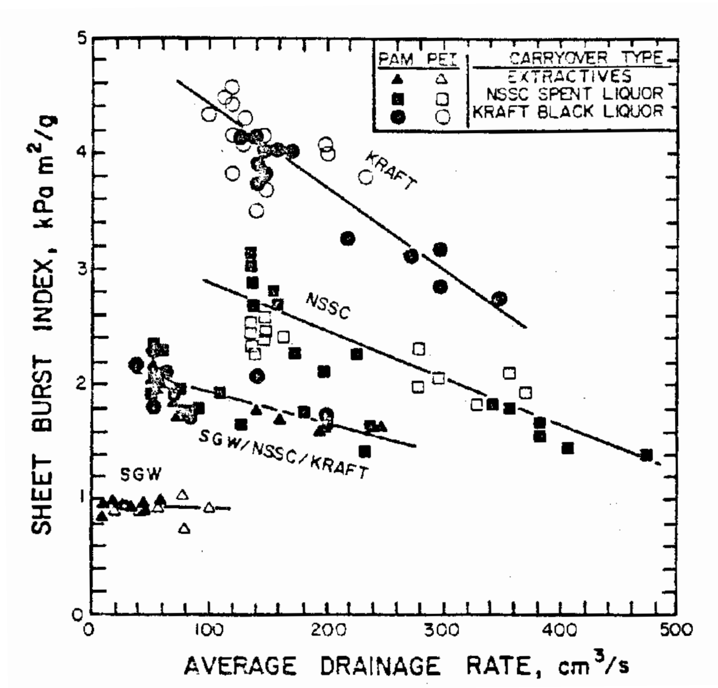

Figure 4. Correlation of burst index and drainage rate far 273 g/m² sheets produced at varying combinations of polymeric additive and pulping carryover levels using dried fiber furnish.

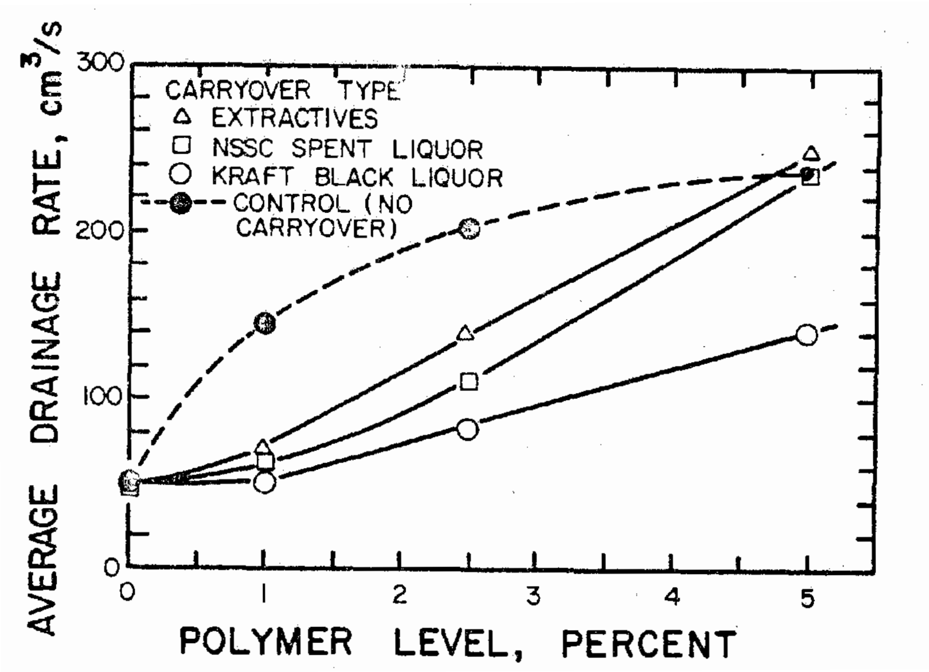

Figure 5. Effect of 1% pulping carryover on polymeric additive (PAM) performance using dried (SGW/NSSC/KRAFT) fiber.

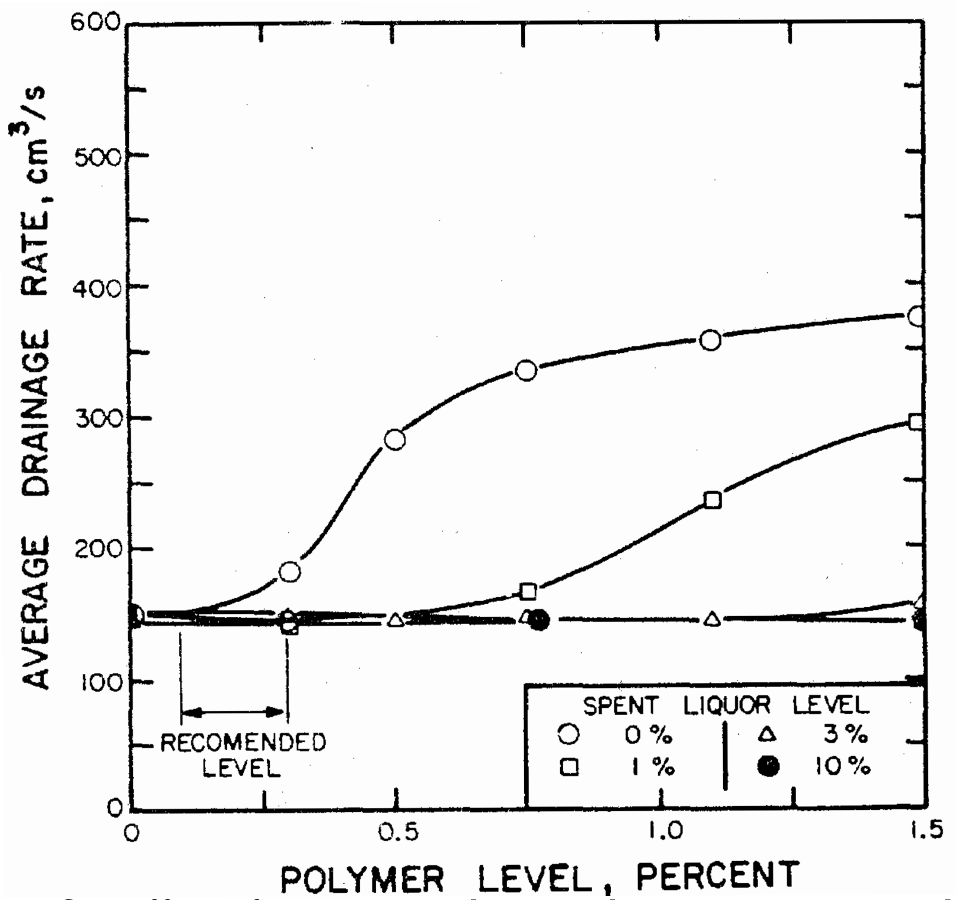

Figure 6. Effect of NSSC spent liquor pulping carryover on polymeric additive (PEI) performance with dried NSSC pulp.

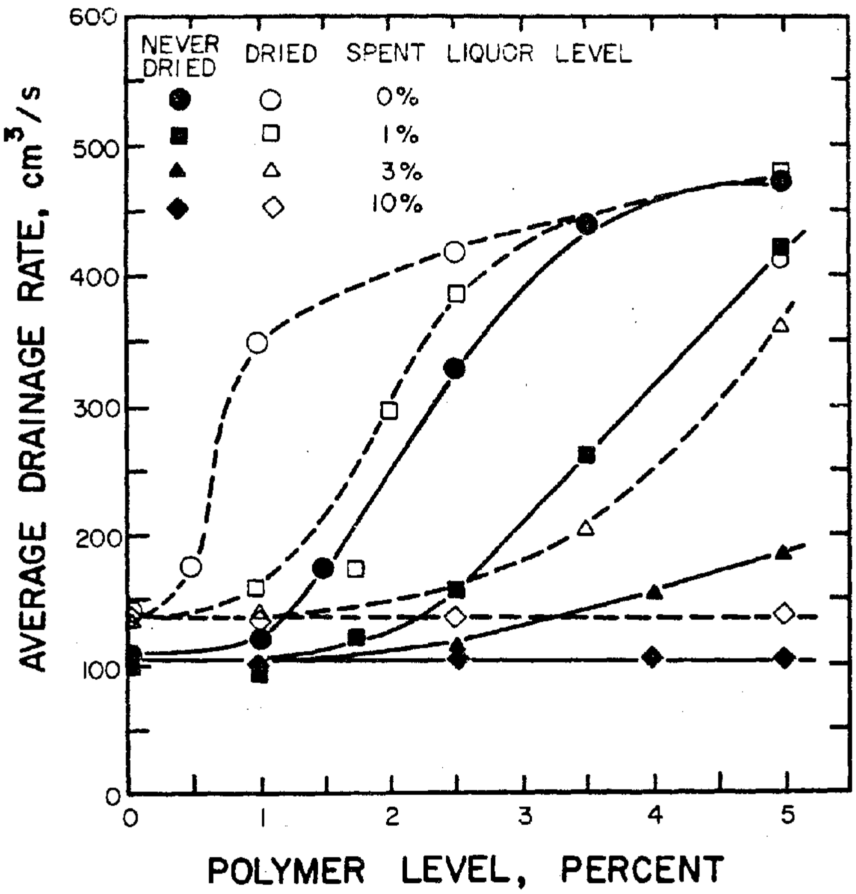

Figure 7. Effect of never-dried vs. dried NSSC fiber furnish on the interaction of PAM and NSSC spent liquor.