

INSTITUTE OF  
PAPER CHEMISTRY  
*Appleton Wisconsin*

**FUNDAMENTALS OF INTERNAL  
STRENGTH ENHANCEMENT  
PART ONE: IMPROVED BONDING VIA  
CHEMICAL ADDITIVES**

**Project 3526**

**Report Two  
A Progress Report  
to**

**MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY**

**September 30, 1986**

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Appleton, Wisconsin

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SUMMARY

Laboratory work completed since issuance of the last progress report<sup>1</sup> consisted of the following units:

1. Evaluation of anionic polymers/PAE (polyamide polyamine epichlorohydrin) in comparisons against CMC (carboxymethyl cellulose)/PAE and PAA (polyacrylic acid)/PAE combinations.
2. The effectiveness of CMC/PAE<sup>2</sup> and PAA/PAE in a wide range of pulps, both whole and classified.
3. The effects of fines and bonding agents in average and high-yield pulps.
4. Analysis of bonding mechanisms.
5. External treatments.

Several anionic polymers other than CMC and PAA were evaluated under Unit 1. The anionic polymers included sodium polystyrene sulfonate (PSFA), sodium alginate, pectins, and carboxymethylated corn (CMCS) and potato starch (CMPS). These materials were tested at total addition levels of approximately 1.0-2.0% based on fiber. The anionic agent/PAE polymer ratio was varied in each case in an effort to establish an optimum ratio for strength properties. CMC/PAE and PAA/PAE were used at the "standard" ratios of 0.4/1.0 and 0.2/1.0, respectively. (Note: Henceforth in this report, the use of CMC/PAE and PAA/PAE will refer to these ratios at addition levels of 1.4 and 1.2%, respectively.) Average yield and 57% yield southern pine unbleached kraft pulps were utilized in this unit.

Results show that synergistic effects occurred in all anionic/PAE combinations, but CMC/PAE proved most effective on an overall basis. Of the new duopolymer systems, carboxymethylated potato starch/PAE proved to be the most interesting, considering performance and economic factors. By way of direct comparison, CMC/PAE provided higher dry and moist breaking lengths than 1:1 CMPS/PAE but the latter proved to be of equal or greater effectiveness in moist Et and STFI compressive strength. Unusually high moist compressive strength factors were obtained with the 57% yield unbleached kraft sheets in the presence of PAE, CMC/PAE, and PAA/PAE. Other results of interest in Unit 1 showed that increasing sheet density via wet pressing failed to match the strength afforded by CMC/PAE or PAA/PAE at roughly equal density.

Under Unit 2, the efficiency of CMC/PAE and PAA/PAE was examined in a wide range of whole and classified pulps including softwood TMP, softwood chemi-mechanical pulp (CMP), softwood bleached kraft, and several samples of softwood unbleached kraft. CMC/PAE was found to be effective in all pulps tested and it was more effective than PAA/PAE in most cases. In turn, PAA/PAE was generally more effective than 1.5% PAE with some exceptions noted in the TMP and a 49% yield kraft pulp. In general, the bonding agents were more effective in the classified pulps when comparisons were made against the controls. However, overall strength was higher in the whole pulps as might be expected. In several cases, classified pulps treated with CMC/PAE approached or equalled the strength of the whole pulps treated in the same manner. It is of interest to note that the bonding agents were more effective in improving strength than stiffness suggesting that stiffness is more dependent on individual fiber modulus than on interfiber bonding.

The study of fines and polymer effectiveness (Unit 3) involved two widely differing pulps, i.e., hemlock TMP and an average yield southern pine unbleached kraft. In the case of the TMP, the readdition of untreated fines to the classified pulp produced dry and moist tensile properties which were roughly comparable to or greater than those of the whole pulp when measured at the same sheet moisture content. The addition of polymer bonding agents to the classified (long) fiber fraction was generally more effective than addition to the fines fraction. Combining CMC/PAE-treated classified fibers and fines to form a whole treated pulp was, in most cases, more effective than adding the same amount of polymer to the original whole pulp. In general, CMC/PAE was more effective than PAA/PAE in this pulp and PAA/PAE was only marginally better than PAE alone. In the case of the unbleached kraft pulp, readdition of fines to the classified pulp failed to match the original whole pulp in strength properties. Once again maximum strength was generally obtained when the polymers were added to the long fiber fraction or to both the long fiber and fines fractions in proportion to their weight. In this case, the duopolymer systems were more effective than PAE in both the classified and whole pulps.

In a continuing study of bonding mechanisms in duopolymer systems (Unit 4) several series of tests were carried out using diffuse reflectance FTIR analysis. Polymers which were capable or incapable of forming covalent bonds with cellulose or with themselves were used in this study. The results revealed that rather substantial strength improvements can be achieved in the absence of covalent bonding; more specifically, in the absence of ester formation. However, the maximum overall strength levels attained under these conditions were lower than those produced by ester formation.

A brief study (Unit 5) was made of the potential for external treatment of paper as opposed to internal treatments which have been the main thrust thus far. The experiments were not necessarily intended to be of commercial applicability but rather to demonstrate a different approach, i.e., one of coating the fibers with a material of high modulus. To this end, 10 and 20% polystyrene in solvent solution was applied to unbleached kraft handsheets (whole pulp). The results show that high moist Et and compressive strength were achieved while maintaining high levels of dry and moist tensile, TEA, and stretch. It would appear, however, that rather substantial add-on levels may be required.

## INTRODUCTION

This is Progress Report Two on Project 3526 entitled, "Fundamentals of Internal Strength Enhancement." This phase of the program is concerned with improved bonding via chemical additives with emphasis directed to moist strength properties including extensional stiffness and compressive strength.

Results in Report One revealed that at least two polymer combinations provided levels of strength which were markedly higher than those of the appropriate controls in classified southern pine unbleached kraft pulps of average yield (47-49%). The additives of primary interest were comprised of combinations of CMC and PAE and of PAA and PAE. In addition to high levels of dry, moist, and wet tensile properties, these combinations also improved Et, stretch, and TEA significantly. The effectiveness of the chemical additives was frequently measured in terms of moist and wet tensile factors which were arbitrarily defined as the breaking length of the treated papers divided by that of the untreated controls. Moist and wet tensile factors for the polymer combinations reached values of 2.6 and 17.0-18.0, respectively, compared to 1.8 and 12.8 for the PAE treated controls. Diffuse reflectance FTIR analysis indicated that covalent bonds are formed in the presence of the polymer combinations.

Supplementary studies indicated that papers containing CMC/PAE and PAA/PAE can be repulped in the laboratory under conditions which approach those used for PAE treated papers with perhaps some modification in time and/or temperature.

The present report extends the work described in Report One to include a) additional anionic polymer/PAE combinations, b) the effectiveness of CMC/PAE and PAA/PAE in a wide range of pulps in whole and classified condition, c) the

effect of fines and duopolymer additives in two pulps differing widely in type and yield, d) further examination of bonding mechanisms in duopolymer systems, and e) external treatments for strength enhancement.

## EXPERIMENTAL PROCEDURES AND RESULTS

## PULPS, HANDSHEET PREPARATIONS, AND TESTING

The pulps used in this part of the program included the following:

1. 57% yield southern pine unbleached kraft; kappa No. 102.3
  2. 47.2% yield southern pine unbleached kraft; kappa No. 34.3
- Note: This pulp was described in Progress Report One and was used to a very limited extent in the current work.
3. 49% yield southern pine unbleached kraft; kappa No. 36.3
  4. Once-dried southern pine unbleached kraft of 46.5-47.0% yield; kappa No. 28 (93% pine; 7% mixed southern hardwoods)
  5. Once-dried hemlock TMP of 88-90% yield
  6. 85-89% yield spruce chemimechanical pulp (CMP)
  7. Once-dried spruce and/or hemlock bleached kraft of average yield

Pulps 1, 2, 3, and 6 were prepared at the Institute whereas Pulps 4, 5, and 7 represent commercial grades. With the exception of the TMP and chemimechanical grades, all pulps were beaten in tap water to 370-410 mL CSF. All or a portion of each pulp was classified (fines removed) on the Institute's continuous web former. The freeness of the classified pulps fell in the range of 700-780 mL CSF. The TMP was beaten 10-15 minutes to remove fiber bundles, resulting in a freeness of 90 mL CSF. Part of the TMP was classified, in which case the resulting freeness was 140 mL CSF. The spruce chemimechanical (CMP) was beaten to 600 mL CSF and a portion was classified on the web former. The freeness of the classified pulp was 770 mL CSF. In several cases, the fines removed on the web former were retained for further study by collecting the white water and

allowing the fines to settle at room temperature over a period of time including several steps of concentration by decantation of the supernatant liquid. All pulps were dewatered to 25-30% solids and stored at 40°F in the presence of a small amount of preservative. The chemical composition of the pulps together with the fiber length distribution and fines content are summarized in Table 1.

Sufficient dewatered pulp to prepare one set of handsheets was redispersed at 1% consistency in tap water by subjecting the suspension to five minutes (600 counts) treatment in a British Disintegrator. The fiber slurry was then diluted with tap water to provide a consistency of 0.5% for subsequent sheetmaking. Each additive was metered as a 1% aqueous solution into the pulp, followed by five minutes of stirring. When used, PAE either alone or cooked in combination with unmodified cornstarch was added to the pulp first followed by the anionic component (Ex. CMC, PAA, etc.). The pH of the fiber-additive mixture was not controlled except in some cases where rosin-alum sizing, pectins, or PAA were used. In these cases the pH was controlled at 4.0 or 4-5 depending upon the additive. In most other cases the pH fell in the range of 7-9. A measured amount of fiber suspension sufficient to form a 2.5 g handsheet was added to a Noble and Wood sheetmold along with additional water so as to provide a forming consistency of 0.04%. The forming wire was 100-mesh monel in all cases. The handsheets were couched from the wire onto blotter stock. Unless specified otherwise, the handsheets were pressed between blotter stock for five minutes at 50 psig and then dried seven minutes in contact with one blotter on a steam drum at 220°F. After conditioning at 50% RH and 73°F, the handsheets were tested for basis weight, density, dry and moist breaking length, tensile energy absorption (TEA), extensional stiffness (Et), and stretch. Wet breaking length was measured after soaking specimens for 24 hours in distilled water. Dry and moist

Table 1. Chemical composition and fiber length distribution of pulps.

Pulp No.	Description	Condition	Hemi-cellulose Content, %	Sugar Content, %				
				Araban, %	Xylan, %	Mannan, Galactan, %	Glucan, %	
1	57% Yield Southern Pine Unbl. Kraft	Classified	16.5	0.9	7.3	5.9	0.4	64.6
3	49% Yield Southern Pine Unbl. Kraft	Classified	17.1	0.8	7.4	6.3	0.5	70.4
3	49% Yield Southern Pine Unbl. Kraft	Whole	--	--	--	--	--	--
4	46-47% Yield Softwood Unbl. Kraft	Classified	19.0	0.7	8.7	6.6	0.8	77.3
4	46-47% Yield Softwood Unbl. Kraft	Whole	19.6	0.9	8.9	6.6	1.0	74.3
5	88-90% Yield Hemlock TMP	Classified	21.4	1.1	5.5	10.6	0.7	45.2
5	88-90% Yield Hemlock TMP	Whole	22.4	1.4	5.9	10.6	1	43.8
5	Fines from above TMP pulp	--	20.4	1.6	5.7	8.6	1.6	37.1
6	85-88% Spruce Chemimechanical (CMP)	Classified	18.2	0.8	5.2	8.2	1.3	48.4
6	85-88% Spruce Chemimechanical (CMP)	Whole	19.1	1.0	5.2	8.3	1.8	46.5
7	Bl. Softwood Kraft	Classified	17.8	0.4	5.2	8.6	0.7	82.8
7	Bl. Softwood Kraft	Whole	17.7	0.4	5.7	8.1	0.8	83.6

Table 1 (Continued). Chemical composition and fiber length distribution of pulps.

Pulp No.	Description	Condition	Lignin Content, %	Ash Content, %	Fiber Length Distribution		Fines Content, a %
					Arithmetic Av., mm	Weighted Av., mm	
1	57% Yield southern pine unbl. kraft	Classified	12.2	0.2	1.4	1.7	--
3	49% Yield southern pine unbl. kraft	Classified	5.0	0.2	2.4	3.0	--
3	49% Yield southern pine unbl. kraft	Whole	--	--	2.4	3.1	15.0
4	46-47% Yield softwood unbl. kraft	Classified	3.7	0.5	1.7	2.4	--
4	46-47% Yield softwood unbl. kraft	Whole	4.1	0.5	1.0	1.8	12.0
5	88-90% Yield hemlock TMP	Classified	24.2	<0.1	1.3	1.7	--
5	88-90% Yield hemlock TMP	Whole	26.7	0.5	1.1	1.3	30.0
5	Fines from above TMP pulp	--	31.3	<0.1	--	--	--
6	85-88% Spruce chemimechanical (CMP)	Classified	26.9	1.4	1.5	1.9	--
6	85-88% Spruce chemimechanical (CMP)	Whole	27.3	1.6	1.0	1.6	12.3
7	Bl. softwood kraft	Classified	0.2	0.2	1.6	2.1	--
7	Bl. softwood kraft	Whole	0.3	0.3	1.1	1.8	9.9

Passed through a 200 mesh screen in a Bauer-McNett classifier.

STFI compressive strength was added to the test list after several units of work had been completed. Sizing (water resistance), when measured, was determined by the fluorescence size or water drop test. "Moist" refers to paper conditioned at high relative humidity, usually 91-93% RH, and 73°F to yield a moisture content of approximately 15-17%. Moist tensile factor is arbitrarily defined as the ratio of the moist breaking length of the treated sheets divided by that of the untreated controls. A similar definition applies to wet tensile and moist compressive strength factors. Note: The average air-dry weight for each set of handsheets was used in determining dry, moist, and wet breaking length.

#### ANIONIC POLYMER/PAE COMBINATIONS

Work with duopolymer systems was extended to include several anionic carboxyl-bearing polymers in combination with PAE. Some of this work was carried out with the classified 57% yield southern pine unbleached kraft (Pulp no. 1). In addition to the reference PAE, CMC/PAE, and PAA/PAE "standards," combinations of sodium polystyrene sulfonate (PSFA)/PAE and alginate/PAE were tested over a range in addition level with a maximum total addition level of 1.6% based on fiber. Results for this series are presented in Table 2 and Fig. 1 to 7. Table 2 also includes results pertaining to the effects of sheet density and sizing agents on sheet properties.

The suggestion was made during the course of the program that pectins might be effective bonding agents for cellulose. Accordingly, the sorptive properties of pectins and related materials in the classified 49% yield southern pine unbleached kraft pulp (Pulp no. 3) were examined. While the results showed rather poor adsorption, the decision was made to pursue the evaluation. Accordingly, pectins and related materials from several sources were incorporated into

Table 2. The effectiveness of additives in a 57% yield classified unbleached softwood kraft pulp, kappa No. 102.3.

Set No.	Additives, % based on fiber	Wet Pressing Conditions	Basis Weight, g/m <sup>2</sup>	Thickness, $\mu$ m	Apparent Density, g/cc	Breaking Length, km	Dry Strength Properties						
							TEA, kgm/m <sup>2</sup>	Et, kg/cm	Stretch, %	SD			
1	Blank controls-1	Normal <sup>a</sup>	62.4	208	0.3	1.54	0.144	0.64	0.143	172	14.9	1.0	0.116
2	Blank controls-2	Flat pressed 15 min at 100 psig	62.7	182	0.345	1.66	0.134	0.805	0.18	179	15.4	1.2	0.149
3	PAE,1.0	Normal	62.1	194	0.32	2.8	0.192	2.3	0.339	195	16.1	1.94	0.161
4	PAE,1.5	Normal	62.3	196	0.318	2.85	0.076	2.03	0.244	234	13.4	1.71	0.188
5	PAE 0.5;PAA,0.1	Normal	62.6	188	0.332	2.88	0.153	2.26	0.366	219	14.3	1.84	0.236
6	1:1 starch:PAE,1.0;PAA,0.1	Normal	63.1	175	0.361	4.15	0.294	4.48	0.584	268	21.7	2.52	0.239
7	PAE,1.0;CMC,0.4	Normal	62.0	182	0.341	3.23	0.239	2.97	0.68	228	9.3	2.2	0.355
8	PAE,1.0;PAA,0.2 <sup>b</sup>	Normal	64.2	178	0.36	4.03	0.323	3.85	1.055	304	25.3	2.23	0.450
9	PAE,1.0;PAA,0.2 <sup>c</sup>	Normal	63.2	187	0.337	3.39	0.302	3.03	0.609	263	17.6	2.12	0.279
10	PAE,1.0;PAA,0.2 <sup>d</sup>	Normal	63.4	199	0.318	2.54	0.175	1.75	0.202	218	12.3	1.66	0.102
11	PAE,1.0;PAA,0.2;alum,0.5; dispersed size,0.25 <sup>d</sup>	Normal	62.7	200	0.314	2.35	0.191	1.65	0.269	204	16.2	1.68	0.122
12	PAE,1.0;PAA,0.2;alkenyl succinic anhydride,0.25 <sup>b</sup>	Normal	61.9	165	0.375	4.47	0.202	4.8	0.538	310	8.2	2.61	0.193
13	PSFA <sup>e</sup> 0.6	Normal	64.9	210	0.309	1.42	0.088	0.592	0.037	176	23.0	0.989	0.069
14	Alginate <sup>f</sup> ,0.6	Normal	62.9	211	0.298	1.27	0.07	0.485	0.082	152	2.1	0.946	0.092
15	PAE,1.0;PSFA,0.1	Normal	61.5	188	0.326	3.13	0.218	2.47	0.452	255	14.6	1.9	0.203
16	PAE,1.0;PSEA,0.2	Normal	61.4	189	0.324	3.14	0.163	2.57	0.558	242	20.2	1.96	0.315
17	PAE,1.0;PSFA,0.4	Normal	62.4	200	0.313	2.68	0.154	1.81	0.285	235	15.9	1.62	0.135
18	PAE,1.0;PSFA,0.6	Normal	61.3	198	0.309	2.56	0.102	1.79	0.291	225	15.5	1.69	0.223
19	PAE,1.0;alginate,0.05	Normal	67.6	210	0.322	2.34	0.257	1.47	0.428	234	8.9	1.4	0.238
20	PAE,1.0;alginate,0.10	Normal	62.8	184	0.341	3.16	0.173	2.58	0.538	262	8.4	1.94	0.266
21	PAE,1.0;alginate,0.20	Normal	64.8	198	0.328	3.11	0.157	2.53	0.321	258	14.3	1.86	0.140
22	PAE,1.0;alginate,0.40	Normal	62.6	193	0.324	2.79	0.245	2.01	0.245	237	5.0	1.71	0.229
23	PAE,1.0;alginate,0.60	Normal	64.7	201	0.322	3.03	0.094	2.48	0.299	255	20.4	1.88	0.173

See end of table for footnotes.

Table 2 (Continued). The effectiveness of additives in a 57% yield classified unbleached softwood kraft pulp, kappa No. 102.3.

Set No.	Additives, % based on fiber	Breaking Length,				Moist Strength Properties				Stretch,		Moist Tensile Factor	Wet Breaking Length		Wet Tensile Factor	Sizing, Water Drop, sec
		km	SD	TEA, kgm/m <sup>2</sup>	SD	Et, kg/cm	SD	%	SD	km	SD					
1	Blank controls-1	0.657	0.031	0.412	0.041	71.5	11.7	1.44	0.193	1.0	0.018	0.004	1.0	Instantaneous		
2	Blank controls-2	0.682	0.036	0.499	0.057	65.8	17.1	1.6	0.12	1.04	0.069	0.008	3.83	Instantaneous		
3	PAE,1.0	1.59	0.11	1.93	0.142	85.3	15.7	2.98	0.27	2.42	0.721	0.043	40.1	Instantaneous		
4	PAE,1.5	1.57	0.107	2.02	0.226	76.0	6.6	3.42	0.084	2.39	0.739	0.029	41.0	Instantaneous		
5	PAE,0.5;PAA,0.1	1.85	0.137	3.13	0.505	97.3	16.6	3.24	0.306	2.82	0.762	0.047	42.3	Instantaneous		
6	1:1 starch:PAA,1.0;PAA,0.1	2.24	0.173	4.23	0.812	109.0	7.97	3.79	0.308	3.41	1.26	0.105	70.0	Instantaneous		
7	PAA,1.0;CMC,0.4	1.87	0.261	2.47	0.674	95.8	5.7	3.42	0.541	2.85	0.994	0.041	55.2	Instantaneous		
8	PAA,1.0;PAA,0.2 <sup>b</sup>	2.26	0.112	3.26	0.179	108.0	18.9	3.65	0.34	3.44	1.13	0.058	62.5	Instantaneous		
9	PAA,1.0;PAA,0.2 <sup>c</sup>	1.97	0.174	2.98	0.36	95.5	15.0	3.6	0.08	3.0	0.913	0.09	50.7	Instantaneous		
10	PAA,1.0;PAA,0.2 <sup>d</sup>	1.38	0.082	1.79	0.177	85.3	13.3	2.92	0.164	2.1	0.721	0.046	40.1	Instantaneous		
11	PAA,1.0;PAA,0.2;alum,0.5; dispersed size,0.25 <sup>d</sup>	1.32	0.085	1.52	0.114	85.0	22.9	2.76	0.12	2.01	0.66	0.06	36.7	1800+		
12	PAA,1.0;PAA,0.2;alkenyl succinic anhydride,0.23 <sup>b</sup>	2.61	0.19	4.01	0.534	98.8	6.15	4.0	0.26	3.97	1.08	0.086	60.0	1800+		
13	PSPAE 0.6	0.379	0.028	0.342	0.022	40.6	3.61	1.72	0.061	0.577	0.046	0.009	2.55	--		
14	Alginatef,0.6	0.378	0.043	0.336	0.059	39.8	2.61	1.67	0.194	0.575	0.0434	0.003	2.41	--		
15	PAA,1.0;PSFA,0.1	1.44	0.079	2.22	0.272	53.3	4.16	3.8	0.237	2.19	0.836	0.05	46.4	Instantaneous		
16	PAA,1.0;PSFA,0.2	1.53	0.076	2.28	0.16	60.2	3.19	3.8	0.135	2.33	0.826	0.061	45.9	Instantaneous		
17	PAA,1.0;PSFA,0.4	1.12	0.078	1.8	0.295	45.1	3.44	3.78	0.19	1.7	0.700	0.023	38.9	Instantaneous		
18	PAA,1.0;PSFA,0.6	1.09	0.081	1.67	0.3	44.0	3.69	3.54	0.406	1.66	0.612	0.043	34.0	Instantaneous		
19	PAA,1.0;alginate,0.05	1.01	0.027	1.42	0.105	47.8	1.22	3.14	0.109	1.54	0.639	0.05	35.5	--		
20	PAA,1.0;alginate,0.10	1.37	0.139	1.94	0.328	59.5	3.22	3.51	0.374	2.08	0.902	0.049	50.1	--		
21	PAA,1.0;alginate,0.20	1.44	0.115	2.05	0.203	62.6	7.22	3.52	0.112	2.19	0.798	0.032	44.3	--		
22	PAA,1.0;alginate,0.40	1.14	0.037	1.57	0.084	40.3	3.8	3.64	0.252	1.74	0.801	0.085	44.5	--		
23	PAA,1.0;alginate,0.60	1.19	0.073	1.72	0.249	50.4	1.85	3.49	0.277	1.81	0.800	0.018	44.4	--		

Set No.	Additives, % based on fiber	Dry STFI Compressive Strength, lb f/inch	Moist STFI Compressive Strength, lb f/inch	Moist Compressive Strength Factor
1	Blank controls-1	3.73	1.87	1.00
3	PAA,1.0	5.68	2.78	1.48
4	PAA,1.5	5.65	2.84	1.52
7	PAA,1.0;CMC,0.4	6.28	2.73	1.46
8	PAA,1.0;PAA,0.2 <sup>b</sup>	6.05	3.06	1.64

<sup>a</sup>Flat pressed 5 min. at 50 psig.  
<sup>b</sup>pH not controlled; final pH 8-9.  
<sup>c</sup>pH adjusted to 5 with sulfuric acid.  
<sup>d</sup>pH adjusted to 5 with alum.  
<sup>e</sup>PSFA = polystyrene sulfonic acid.  
<sup>f</sup>Sodium alginate, medium viscosity.

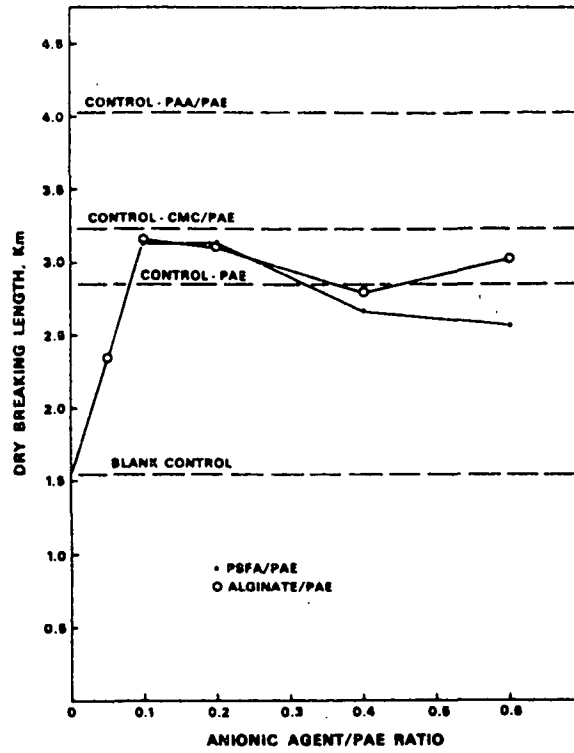


Figure 1. The effect of additive ratio on dry breaking length. (57% yield softwood unbleached kraft - classified).

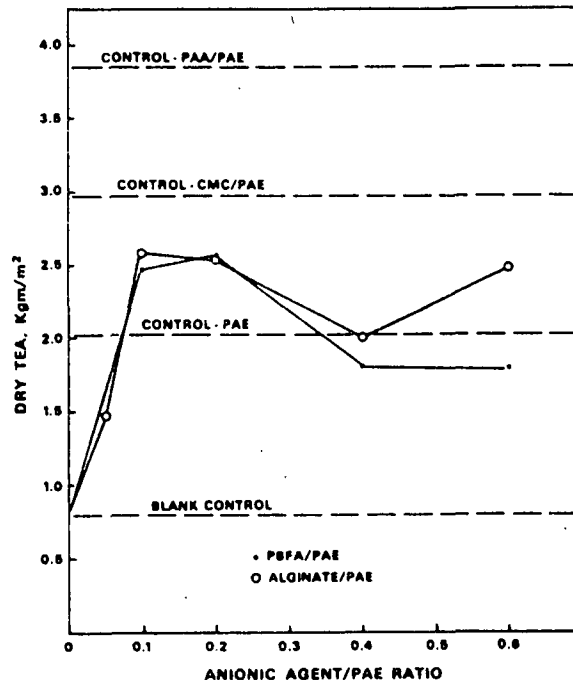


Figure 2. The effect of additive ratio on dry TEA. (57% yield softwood unbleached kraft - classified).

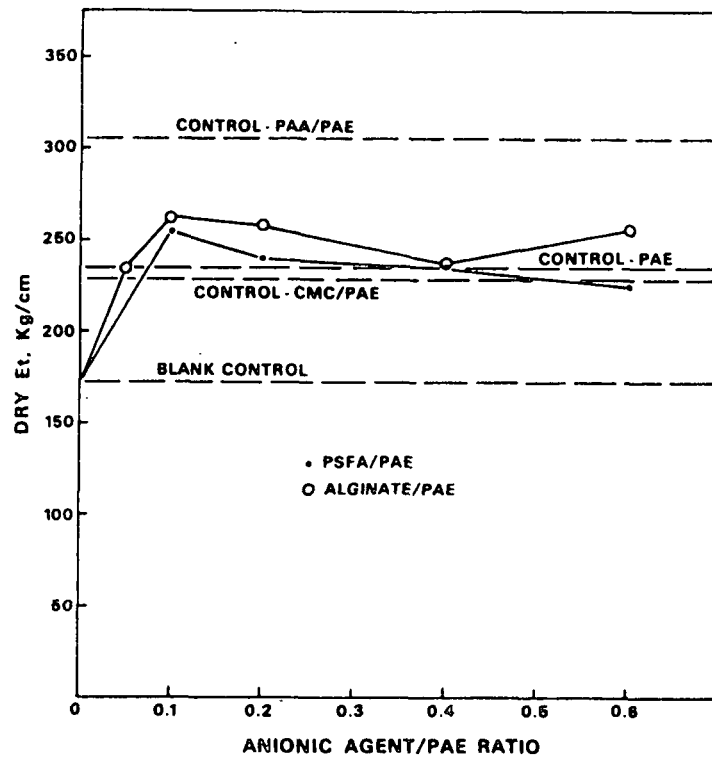


Figure 3. The effect of additive ratio on dry Et (57% yield softwood unbleached kraft - classified).

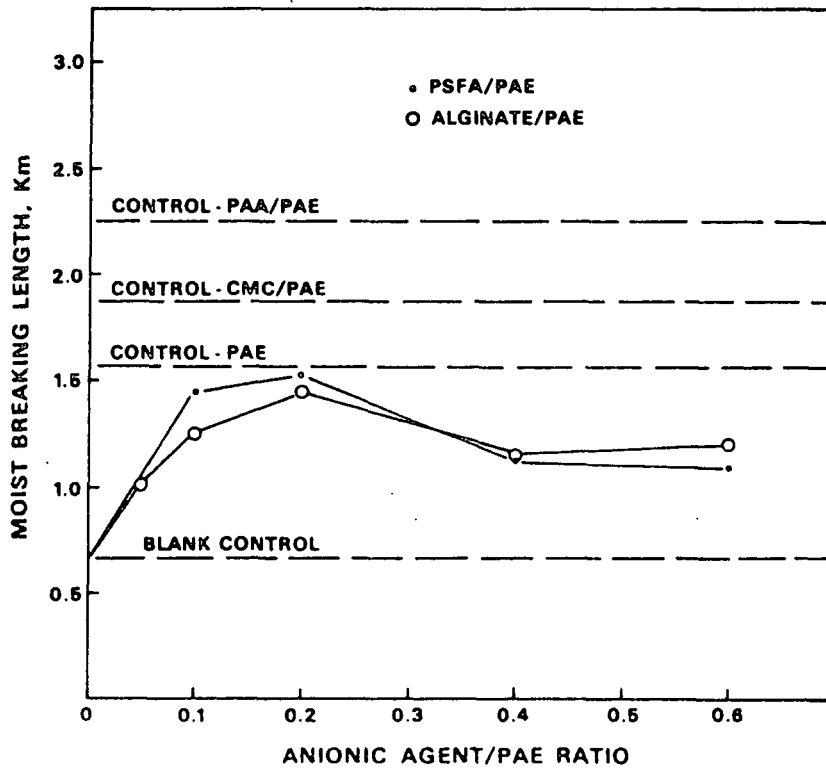


Figure 4. The effect of additive ratio on moist breaking length (57% yield softwood unbleached kraft - classified).

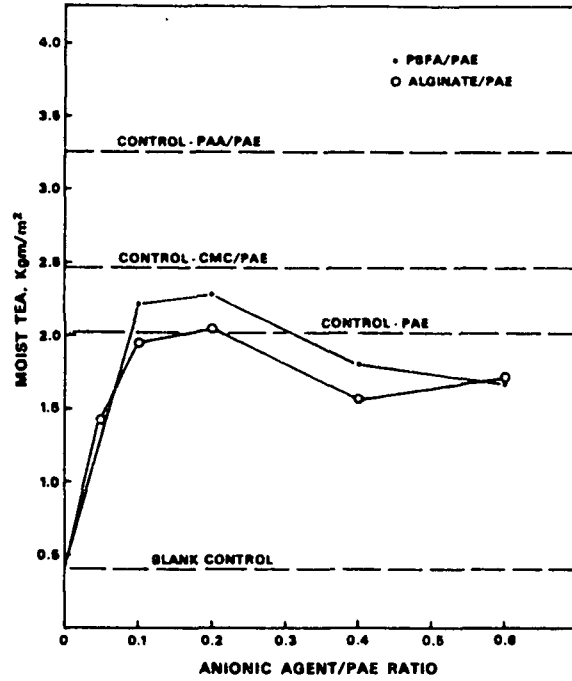


Figure 5. The effect of additive ratio on moist TEA (57% yield softwood unbleached kraft - classified).

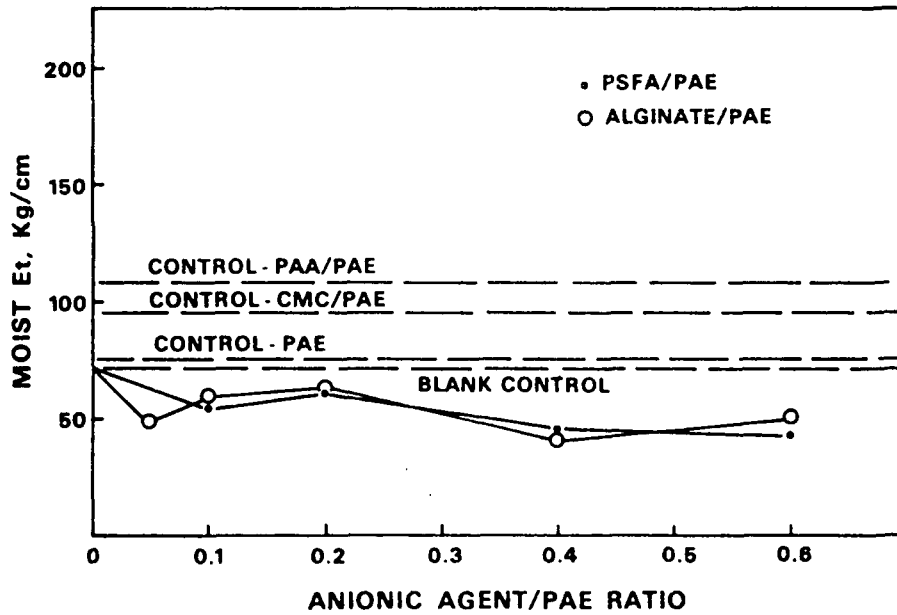


Figure 6. The effect of additive ratio on moist Et (57% yield softwood unbleached kraft - classified).

Pulp No. 3 at an addition level of 2%. The results of the strength tests which are presented in Table 3 clearly indicate that pectins, by themselves, are poor bonding agents. However, since pectins are anionic polymers, the decision was made to add pectins in combination with PAE as had been done with CMC, alginate, etc. The results of these tests are presented in Table 4, and strength properties as a function of pectin/PAE ratio are presented in Fig. 8 to 13.

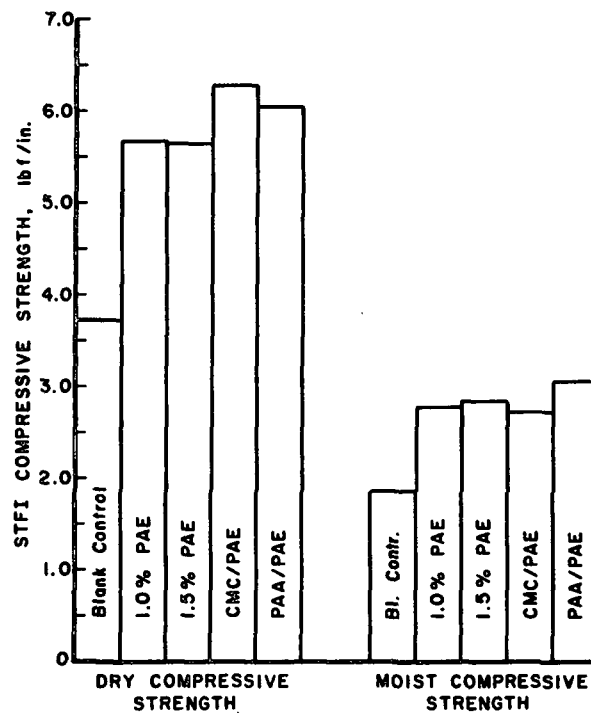


Figure 7. STFI compressive strength - classified, 57% yield softwood unbleached kraft.

Table 3. A comparison of pectins as bonding agents for southern pine unbleached kraft, (49% yield-classified).

Set No.	Additives, % based on fiber	Basis Weight, g/m <sup>2</sup>	Thick-ness, $\mu$ m	Apparent Density, g/cc	Dry Strength Properties			Moist Strength Properties				
					Breaking Length, km	TEA, kgm/m	Et, kg/cm	Breaking Length, km	TEA, kgm/m <sup>2</sup>	Et, Kg/cm	Moist Tensile Factor	Wet Breaking Length, Km
24	Blank controls	63.1	158	0.399	3.93	0.212	4.37	0.282	279	14.7	2.58	0.052
25	PAE,1.0	67.3	174	0.387	5.73	0.279	6.92	0.847	450	16.9	2.76	0.241
26	PAE,1.5	71.7	166	0.433	6.12	0.794	8.99	1.166	412	58.4	3.13	0.216
27	PAE,1.0;CMC,0.4	63.9	152	0.419	7.79	0.372	11.2	1.19	355	16.0	3.58	0.232
28	PAE,1.0;PAA,0.2	71.9	167	0.43	6.48	0.109	9.05	0.851	379	50.5	3.0	0.249
29	1:1 starch:PAE,1.0;PAA,0.1	70.5	164	0.428	6.13	0.549	9.16	1.29	375	48.6	3.27	0.166
30	Grape fruit pectin, 2.0	68.8	167	0.411	3.61	0.343	3.59	0.648	307	22.6	2.12	0.195
31	Pectin from citrus fruits;No. P-9135,2.0	69.0	167	0.413	3.99	0.285	4.43	0.634	312	16.8	2.37	0.166
32	Sunkist polygalacturonic acid, No. 3491,2.0	72.8	176	0.413	3.95	0.351	4.84	0.689	337	33.8	2.46	0.149
33	Polygalacturonic acid from orange;No. 3889,2.0	62.3	158	0.345	3.87	0.269	3.74	0.559	270	56.7	2.28	0.206
34	Sugar beet pectin,2.0	67.9	167	0.406	3.47	0.379	3.28	0.594	334	38.7	2.0	0.163
35	Guar gum No. 4129;Lot 21-F-0521,2.0	64.5	153	0.42	4.48	0.194	5.54	0.53	326	19.1	2.82	0.189

Set No.	Additives, % based on fiber	Moist Strength Properties			Dry Strength Properties			Moist Tensile Factor	Wet Breaking Length, Km	Wet Tensile Factor			
		Breaking Length, km	TEA, kgm/m <sup>2</sup>	Et, Kg/cm	Breaking Length, km	TEA, kgm/m	Et, kg/cm						
24	Blank controls	1.98	0.114	2.68	0.186	109	6.9	3.39	0.073	1.0	0.158	0.012	1.0
25	PAE,1.0	3.37	0.359	5.99	0.627	148	11.6	4.32	0.277	1.7	1.69	0.044	10.69
26	PAE,1.5	3.79	0.327	6.65	0.492	131	11.2	4.59	0.121	2.0	1.92	0.119	12.15
27	PAE,1.0;CMC,0.4	4.86	0.311	9.05	1.076	150	23.4	5.16	0.253	2.45	2.27	0.2	14.37
28	PAE,1.0;PAA,0.2	4.05	0.331	7.51	0.96	172	21.4	4.41	0.206	2.05	1.81	0.062	11.45
29	1:1 starch:PAE,1.0;PAA,0.1	3.9	0.268	6.96	0.797	190	23.7	4.29	0.262	1.97	1.35	-----	8.54
30	Grape fruit pectin,2.0	2.1	0.236	3.17	0.54	163	13.3	3.3	0.193	1.06	0.13	0.022	0.82
31	Pectin from citrus fruits;No. P-9135,2.0	2.08	0.05	2.84	0.198	159	8.3	3.05	0.165	1.05	0.115	0.0126	0.73
32	Sunkist polygalacturonic acid, No. 3491,2.0	2.25	0.294	3.45	0.744	179	22.0	3.18	0.277	1.14	0.14	0.027	0.89
33	Polygalacturonic acid from orange;No. 3889,2.0	2.13	0.124	2.94	0.186	139	17.0	3.37	0.073	1.08	0.148	0.0081	0.94
34	Sugar beet pectin, 2.0	1.95	0.128	2.63	0.192	162	11.1	2.94	0.059	0.98	0.132	0.015	0.84
35	Guar gum No. 4129;Lot 21-F-0521,2.0	2.39	0.077	3.36	0.062	174	12.5	3.36	0.084	1.2	0.166	0.0076	1.05

Table 4. The effect of selected pectins on the strength properties of unbleached southern pine kraft; yield 49.2%; beaten and classified.

Set No.	Additives, % based on fiber	Basis Weight, g/m <sup>2</sup>	Thick-ness, $\mu$ m	Apparent Density, g/cc	Dry Strength Properties				Moist Strength Properties								
					Breaking Length, km	SD	TEA, kgm/m <sup>2</sup>	SD	Et, kg/cm	SD	Stretch, %	SD	Wet Tensile Factor	Wet Breaking Length, km	SD	Wet Tensile Factor	
24	Blank controls	63.1	158	0.399	3.93	0.212	4.37	0.282	279	14.7	2.58	0.052					
25	PAE, 1.0	67.3	174	0.387	5.73	0.279	6.92	8.47	350	16.9	2.76	0.244					
26	PAE, 1.5	71.7	166	0.433	6.12	0.794	8.99	1.166	412	58.4	3.13	0.266					
27	PAE, 1.0; CMC, 0.4	63.9	152	0.419	7.79	0.372	11.2	1.119	355	16.0	3.58	0.232					
28	PAE, 1.0; PAA, 0.2	71.9	167	0.43	6.48	0.109	9.05	0.851	379	50.5	3.0	0.249					
29	1:1 starch; PAE, 1.0; PAA, 0.1	70.5	164	0.428	6.13	0.549	9.16	1.29	375	48.6	3.26	0.166					
36	Pectin P-9135a, 2.0; alum to pH 4.0	72.9	172	0.423	3.8	0.11	4.36	0.385	305	62.2	2.36	0.157					
37	Pectin P-9135a, 2.0; alum to pH 5.5	71.0	170	0.419	3.92	0.364	4.35	0.892	358	24.1	2.24	0.263					
38	Pectin P-9135a, 2.0; alum to pH 7.0	66.5	162	0.412	3.84	0.29	3.84	0.852	315	20.0	2.19	0.232					
39	PAE, 1.0; pectin P-9135, 0.1	67.6	162	0.417	6.31	0.317	8.27	0.411	382	20.8	3.02	0.038					
40	PAE, 1.0; pectin P-9135, 0.2	74.7	172	0.434	6.69	0.495	10.5	1.24	436	28.5	3.27	0.189					
41	PAE, 1.0; pectin P-9135, 0.4	62.8	145	0.434	6.63	0.63	10.8	1.4	375	30.0	3.59	0.165					
42	PAE, 1.0; pectin P-9135, 0.6	67.8	152	0.447	7.58	0.453	12.1	0.99	415	33.1	3.72	0.167					
43	PAE, 1.0; pectin P-9135, 1.0	71.0	156	0.454	7.35	0.372	10.8	1.34	455	11.4	3.26	0.245					
44	PAE, 1.0; sugar beet pectin, 0.1	71.5	169	0.424	5.47	0.694	6.92	1.85	375	21.4	2.73	0.415					
45	PAE, 1.0; sugar beet pectin, 0.4	73.5	172	0.428	6.27	0.226	9.48	0.759	410	10.2	3.23	0.165					
46	PAE, 1.0; sugar beet pectin, 1.0	68.4	160	0.425	6.64	0.538	9.50	1.203	394	24.8	3.28	0.165					
Set No.	Additives, % based on fiber	Breaking Length, km	SD	TEA, kgm/m <sup>2</sup>	SD	Et, kg/cm	SD	Stretch, %	SD	Wet Tensile Factor	Wet Breaking Length, km	SD	Wet Tensile Factor				
24	Blank controls	1.98	0.114	2.68	0.186	109	6.9	3.39	0.073	1.0	0.158	0.012	1.0				
25	PAE, 1.0	3.37	0.359	5.99	0.627	148	11.6	4.32	0.277	1.7	1.69	0.044	10.69				
26	PAE, 1.5	3.79	0.437	6.65	0.492	131	11.2	3.59	0.121	1.9	1.92	0.119	12.15				
27	PAE, 1.0; CMC, 0.4	4.86	0.311	9.05	1.076	150	23.4	5.1	0.253	2.45	2.27	0.2	14.37				
28	PAE, 1.0; PAA, 0.2	4.05	0.331	7.51	0.96	172	21.4	4.41	0.206	2.05	1.81	0.062	11.45				
29	1:1 starch; PAE, 1.0; PAA, 0.1	3.9	0.268	6.96	0.797	190	23.7	4.29	0.262	1.97	1.35		8.54				
36	Pectin P-9135a, 2.0; alum to pH 4.0	2.18	0.065	3.75	0.132	160	8.7	3.52	0.181	1.1	0.143	0.0028	0.91				
37	Pectin P-9135a, 2.0; alum to pH 5.5	2.05	0.129	3.25	0.133	138	12.0	3.51	0.088	1.01	0.149	0.021	0.94				
38	Pectin P-9135a, 2.0; alum to pH 7.0	1.99	0.141	3.01	0.298	123	7.1	3.6	0.149	1.0	0.138	0.011	0.87				
39	PAE, 1.0; pectin P-9135, 0.1	3.78	0.169	7.61	0.668	135	12.2	4.59	0.228	1.91	1.91	0.126	12.09				
40	PAE, 1.0; pectin P-9135, 0.2	4.04	0.318	7.69	1.059	131	10.4	5.03	0.314	2.04	1.95	0.101	12.34				
41	PAE, 1.0; pectin P-9135, 0.4	4.78	0.392	8.02	0.808	140	14.0	4.93	0.169	2.4	2.27	0.186	14.37				
42	PAE, 1.0; pectin P-9135, 0.6	4.79	0.339	8.24	1.103	153	9.5	4.88	0.269	2.42	2.32	0.225	14.68				
43	PAE, 1.0; pectin P-9135, 1.0	4.73	0.287	8.76	1.279	138	9.4	5.08	0.361	2.39	2.32	0.097	14.68				
44	PAE, 1.0; sugar beet pectin, 0.1	3.62	0.262	7.37	7.51	120	7.3	4.68	0.268	1.83	1.77	0.046	11.2				
45	PAE, 1.0; sugar beet pectin, 0.4	3.74	0.141	7.88	0.454	129	8.3	4.65	0.25	1.89	1.82	0.118	11.52				
46	PAE, 1.0; sugar beet pectin, 1.0	4.08	0.214	8.85	0.251	117	10.3	5.04	0.137	2.06	1.89	0.106	11.96				

pectin from citrus fruits.

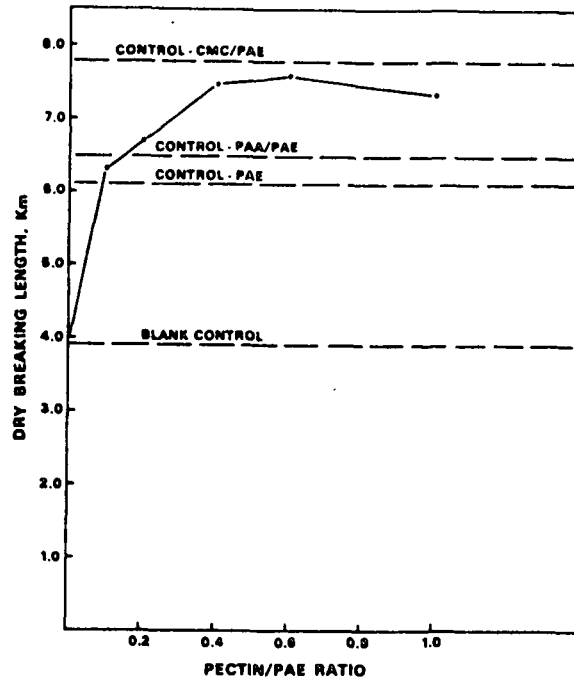


Figure 8. The effect of fruit pectin/PAE ratio on dry breaking length (49% yield softwod unbl. kraft - classified).

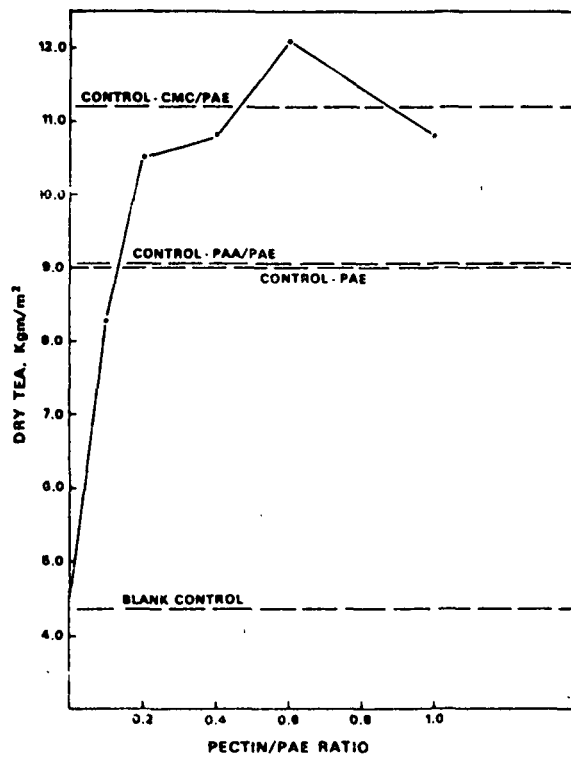


Figure 9. The effect of fruit pectin/PAE ratio on dry TEA (49% yield softwod unbl. kraft - classified).

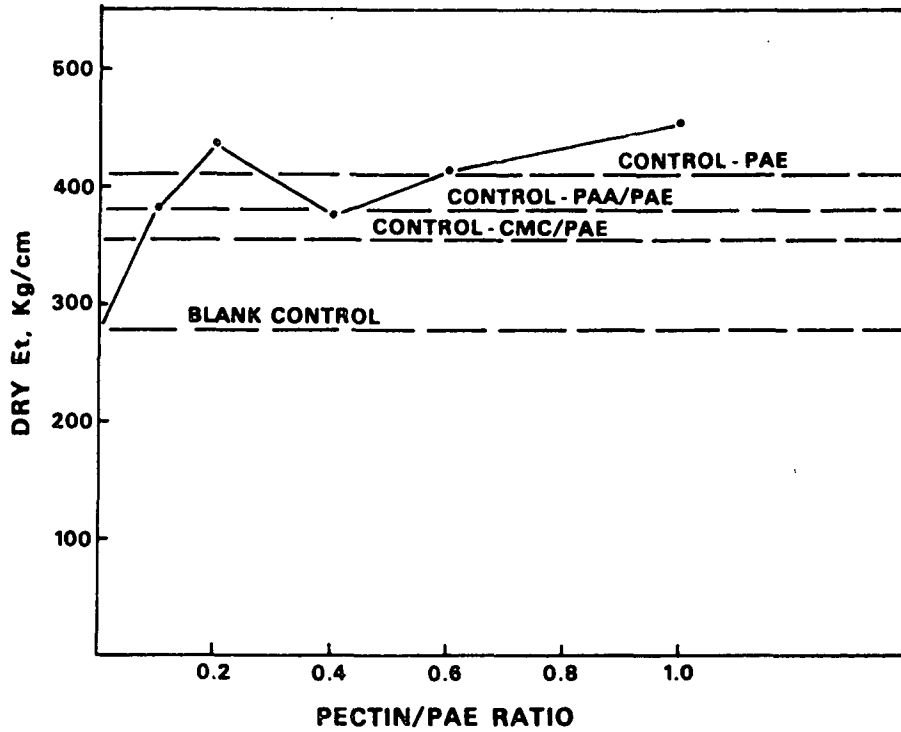


Figure 10. The effect of fruit pectin/PAE ratio on dry Et (49% yield softwood unbl. kraft - classified).

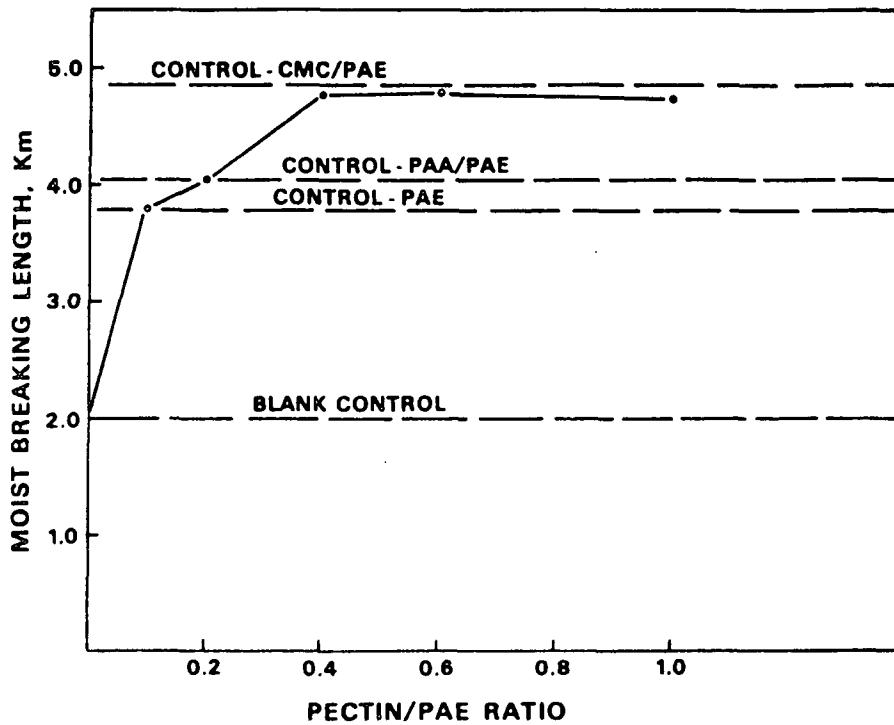


Figure 11. The effect of fruit pectin/PAE ratio on moist breaking length (49% yield softwood unbl. kraft - classified).

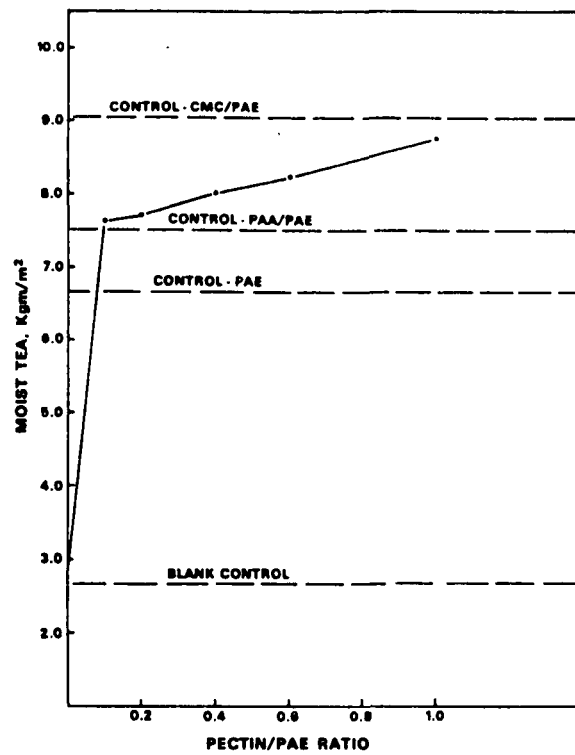


Figure 12. The effect of fruit pectin/PAE ratio on moist TEA (49% yield softwood unbl. kraft - classified).

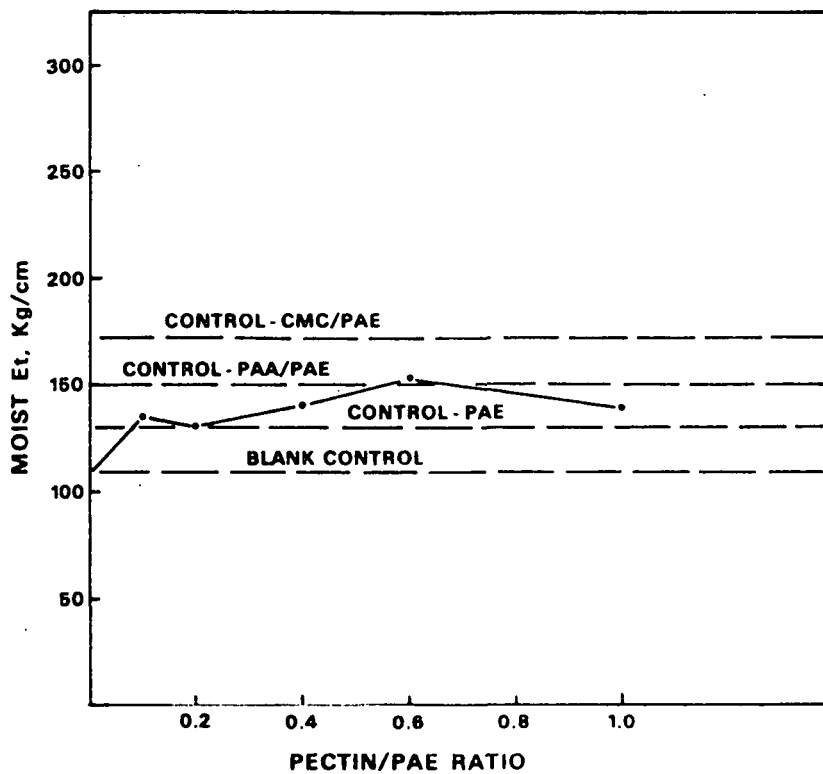


Figure 13. The effect of fruit pectin/PAE ratio on moist Et (49% yield softwood unbl. kraft - classified).

A third series involving anionic polymer/PAE combinations used carboxymethylated starch in the once-dried, classified unbleached kraft pulp (Pulp No. 4). This unit consisted of the addition of carboxymethylated corn and potato starches, each over a range in starch/PAE ratio. The starches were prepared by heating the aqueous suspension for 20 min. at 95°C. Results of the physical tests for this series are presented in Table 5, and selected strength properties as a function of starch/PAE ratio are shown in Fig. 14 to 18.

Note: The evaluation of the anionic polymer/PAE combinations was carried out over an extended period of time (approx. 1 yr.). Accordingly, it was necessary to change pulps, since some supplies were exhausted in the interim. This is also the reason for slight differences in the physical tests employed.

#### EFFICIENCY OF CMC/PAE and PAA/PAE IN WHOLE AND CLASSIFIED PULPS

This unit will overlap the first, since some of the same bonding agents and pulps were used in both cases. The work is intended to compare the effectiveness of the reference "standard" bonding agents in the classified and whole pulps or, in effect, to show the general influence of fines on polymer effectiveness. A more complete study of fines polymer interactions comprises the subject matter of the next unit.

The first series of comparisons involved the use of the hemlock TMP (Pulp No. 5), and the physical test results are presented in Table 6. Bar graphs showing breaking length and Et for the whole and classified pulps are presented in Fig. 19 to 23.

Table 5. The effectiveness of carboxymethylated starch as a bonding agent in combination with PAE (once-dried classified softwood unbleached kraft).

Set No.	Additives, % based on fiber	Basis Wt., g/m <sup>2</sup>	Apparent Density, g/cc	Dry Strength Properties							
				Breaking Length, km		TEA, kgm/m <sup>2</sup>		Et, kg/cm		Stretch, %	
				Av.	SD	Av.	SD	Av.	SD	Av.	SD
47	Blank control	62.9	0.447	3.83	0.284	4.51	0.563	316	33.5	2.6	0.26
48	PAE, 1.0	65.8	0.442	5.27	0.361	7.46	0.954	357	26.6	3.2	0.21
49	PAE, 1.5	61.4	0.447	5.38	0.368	7.64	1.236	313	5.7	3.5	0.36
50	PAE, 1.0; CMC, 0.4	64.9	0.484	7.27	0.531	12.2	1.41	409	22.2	4.0	0.22
51	PAE, 1.0; PAA, 0.2	64.7	0.466	6.14	0.380	0.4	1.01	368	24.9	3.9	0.27
52	PAE, 1.0; anionic starch <sup>a</sup> 1.5	65.4	0.477	5.87	0.368	8.93	0.867	339	32.7	3.5	0.26
53	PAE, 1.0; anionic starch <sup>a</sup> 1.0	68.3	0.456	6.10	0.176	10.1	0.94	367	16.4	3.7	0.27
54	PAE, 1.0; anionic starch <sup>a</sup> 0.5	69.9	0.462	5.99	0.605	10.7	1.32	361	36.9	3.8	0.13
55	PAE, 1.0; anionic starch <sup>a</sup> 0.2	66.7	0.461	5.90	0.293	9.14	0.962	360	25.3	3.5	0.33
56	PAE, 1.0; anionic starch <sup>b</sup> 1.0	73.2	0.492	6.32	0.350	12.3	1.07	407	40.8	3.9	0.16
57	PAE, 1.0; anionic starch <sup>b</sup> 0.5	65.6	0.461	6.38	0.302	10.3	0.54	368	25.4	3.7	0.13
58	PAE, 1.0; anionic starch <sup>b</sup> 0.2	67.2	0.460	5.91	0.521	9.08	1.674	369	20.8	3.4	0.37
59	Anionic starch <sup>a</sup> control, 1.0	60.7	0.423	3.51	0.124	4.06	0.288	272	14.4	2.6	0.10
60	Anionic starch <sup>b</sup> control, 1.0	60.3	0.427	3.61	0.213	4.14	0.530	274	11.5	2.6	0.17

See end of table for footnotes.

Table 5 (Continued). The effectiveness of carboxymethylated starch as a bonding agent in combination with PAE (once-dried classified softwood unbleached kraft).

Set No.	Additives, % based on fiber	Moisture Content, % at 91-93% RH	Moist Strength Properties						Moist Tensile Factor	Wet Breaking Length, km Av.	Wet Tensile Factor		
			Breaking Length, km Av.	TEA, kgm/cm <sup>2</sup> Av.	Et, kg/cm Av.	Stretch, % Av.	Wet Breaking Length, km SD	TEA, kgm/cm <sup>2</sup> SD				Et, kg/cm SD	Stretch, % SD
47	Blank control	15.9	1.88	3.09	0.354	111	9.3	3.9	0.40	1.0	0.129	0.008	1.00
48	PAE, 1.0	15.2	3.64	7.74	1.03	129	5.1	5.1	0.35	1.94	1.27	0.152	9.8
49	PAE, 1.5	14.8	3.73	7.54	0.557	120	7.6	5.3	0.28	1.98	1.66	0.095	12.9
50	PAE, 1.0; CMC, 0.4	15.5	4.78	11.92	1.05	142	5.5	6.2	0.28	2.54	2.30	0.138	17.8
51	PAE, 1.0; PAA, 0.2	15.5	4.17	9.21	0.718	125	11.9	5.8	0.30	2.22	1.73	0.112	13.4
52	PAE, 1.0; anionic starch <sup>a</sup> 1.5	13.9	3.84	7.30	1.200	144	10.2	5.3	0.41	2.04	1.41	0.116	10.9
53	PAE, 1.0; anionic starch <sup>a</sup> 1.0	14.9	3.89	7.75	0.625	136	7.7	5.5	0.33	2.07	1.61	0.096	12.5
54	PAE, 1.0; anionic starch <sup>a</sup> 0.5	15.1	3.84	8.55	0.837	142	15.0	5.5	0.14	2.04	1.53	0.155	11.9
55	PAE, 1.0; anionic starch <sup>a</sup> 0.2	14.7	3.90	8.59	0.795	156	14.5	5.2	0.19	2.07	1.67	0.128	12.9
56	PAE, 1.0; anionic starch <sup>b</sup> 1.0	14.9	4.44	11.6	0.94	187	11.5	5.8	0.12	2.36	1.84	0.121	14.3
57	PAE, 1.0; anionic starch <sup>b</sup> 0.5	15.7	3.72	7.60	1.625	142	7.7	5.2	0.57	1.98	1.73	0.130	13.4
58	PAE, 1.0; anionic starch <sup>b</sup> 0.2	15.7	3.42	6.97	2.880	125	10.7	5.3	0.86	1.82	1.66	0.161	12.8
59	Anionic starch <sup>a</sup> control, 1.0	15.7	1.80	3.00	0.346	108	4.7	3.6	1.00	0.96	0.0781	0.006	0.61
60	Anionic starch <sup>b</sup> control, 1.0	15.4	1.79	3.06	0.316	110	3.1	4.0	0.18	0.95	0.0847	0.002	0.66

See end of table for footnotes.

Table 5 (Continued). The effectiveness of carboxymethylated starch as a bonding agent in combination with PAE (once-dried classified softwood unbleached kraft).

Set No.	Additives, % based on fiber	Dry STFI		Moist STFI		Moist Compressive Strength Factor
		Strength, lb f/inch Av.	SD	Strength, lb f/inch Av.	SD	
47	Blank control	7.13	0.777	2.89	0.208	1.00
48	PAE, 1.0	8.79	0.872	3.01	0.490	1.04
49	PAE, 1.5	8.36	0.777	3.02	0.291	1.04
50	PAE, 1.0; CMC, 0.4	10.12	0.813	3.75	0.326	1.30
51	PAE, 1.0; PAA, 0.2	8.97	0.641	3.41	0.388	1.18
52	PAE, 1.0; anionic starch <sup>a</sup> 1.5	9.21	0.903	3.33	0.314	1.15
53	PAE, 1.0; anionic starch <sup>a</sup> 1.0	9.22	0.931	3.45	0.323	1.19
54	PAE, 1.0; anionic starch <sup>a</sup> 0.5	9.90	0.819	3.72	0.403	1.29
55	PAE, 1.0; anionic starch <sup>a</sup> 0.2	8.92	0.675	3.87	0.451	1.34
56	PAE, 1.0; anionic starch <sup>b</sup> 1.0	11.03	1.024	3.95	0.477	1.37
57	PAE, 1.0; anionic starch <sup>b</sup> 0.5	8.93	0.926	3.39	0.314	1.17
58	PAE, 1.0; anionic starch <sup>b</sup> 0.2	8.37	0.624	3.94	0.362	1.36
59	Anionic starch <sup>a</sup> control, 1.0	5.93	0.500	2.68	0.200	0.93
60	Anionic starch <sup>b</sup> control, 1.0	6.05	0.519	2.89	0.247	1.00

<sup>a</sup>Corn starch-carboxymethyl content; 1.2% min.

<sup>b</sup>Potato starch-carboxymethyl content; 1.4% min.

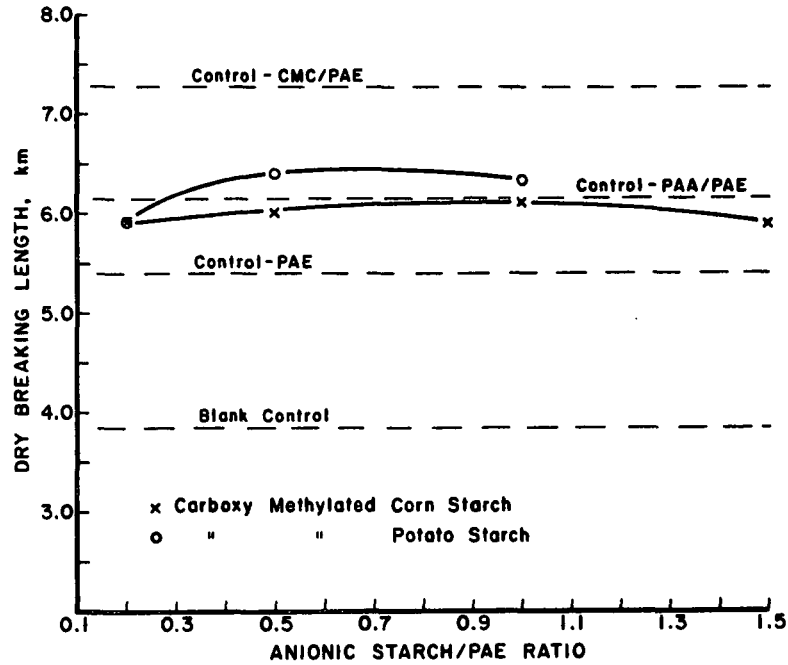


Figure 14. The effect of anionic starch/PAE ratio on dry breaking length (classified softwood unbl. kraft - Pulp No. 4).

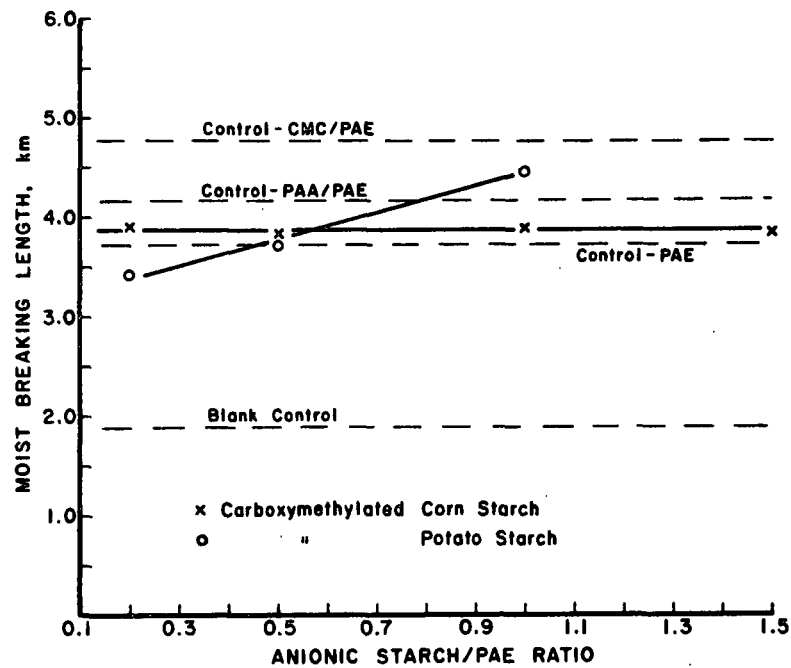


Figure 15. The effect of anionic starch/PAE ratio on moist breaking length (classified softwood unbl. kraft - Pulp No. 4).

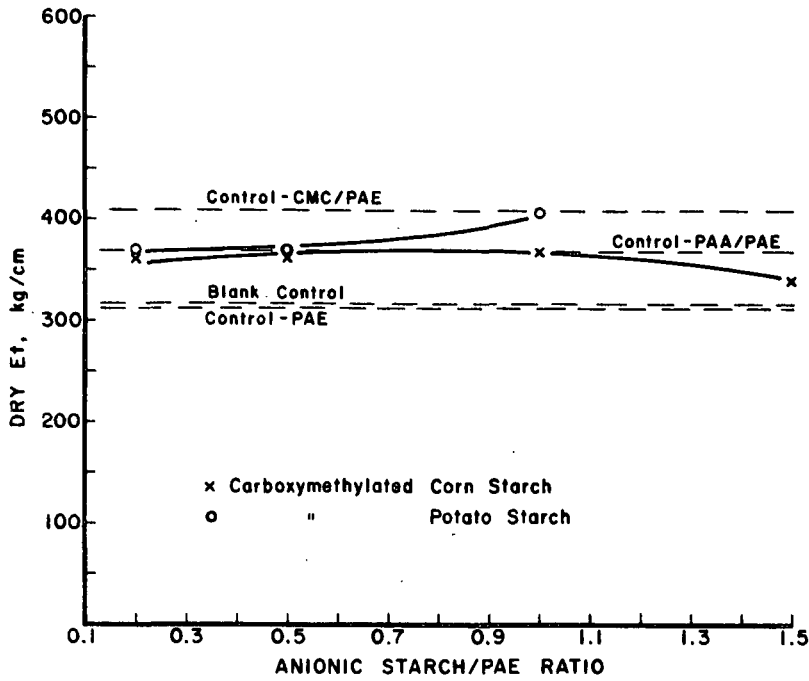


Figure 16. The effect of anionic starch/PAE ratio on dry Et (classified softwood unbl. kraft - Pulp No. 4).

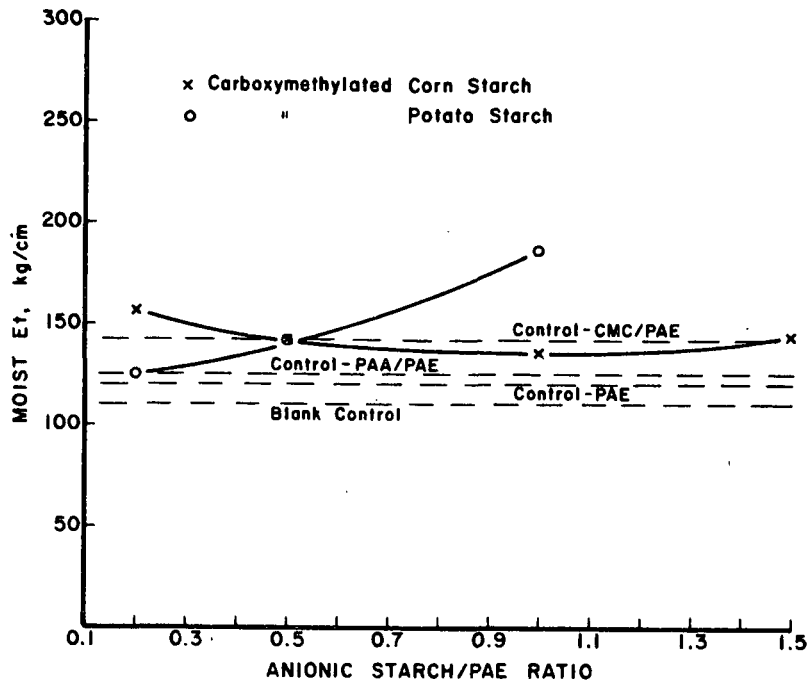


Figure 17. The effect of anionic starch/PAE ratio on moist Et (classified softwood unbl. kraft - Pulp No. 4).

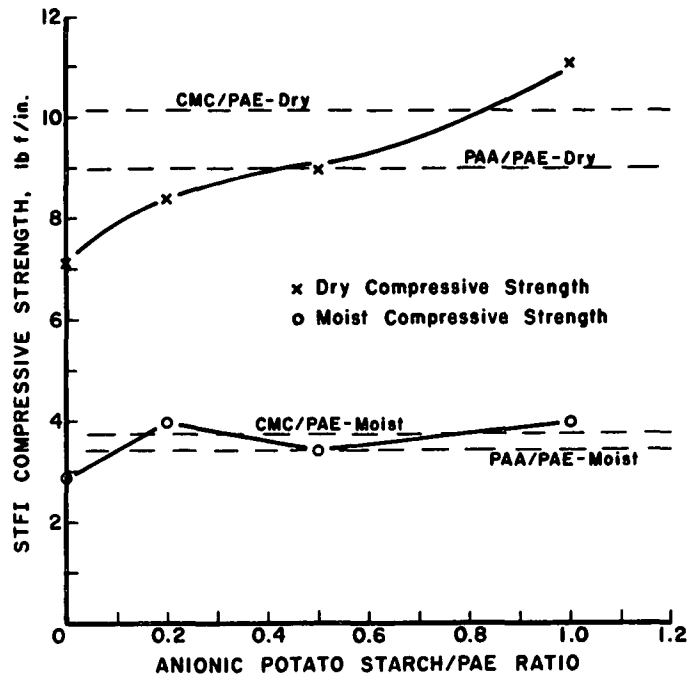


Figure 18. The effect of anionic potato starch/PAE ratio on STFI compressive strength (classified softwood unbleached kraft - Pulp No. 4).

The second comparison of classified and whole pulps involved the 49% yield southern pine unbleached kraft (Pulp No. 3). The results for the series are presented in Table 7. Since the polyacrylic acid used in this program is rather strongly acidic and since pH will affect ionization, the decision was made to compare PAA/PAE effectiveness at pH 7-9 and at pH 4.5-5.0. Results are presented in Table 8. Bar graphs showing breaking length, Et, and STFI compressive strength are presented in Fig. 24 to 29.

Subsequent comparisons included the once-dried softwood unbleached kraft (Pulp No. 4), the spruce chemimechanical pulp (Pulp No. 6), and the softwood bleached kraft (Pulp No. 7). The latter comparison included a series incorporating carboxymethylated fiber as part of the total fibrous component. Physical test results for these pulps are presented in Tables 9-11, and the bar graphs are shown in Fig. 30 to 47. The effect of fibrous CMC content on the strength properties of the bleached kraft pulp is shown in Fig. 48 to 49.

Table 6. The effectiveness of bonding agents in softwood TMP.

Set No.	Additives, % based on fiber	Basis Wt., g/m <sup>2</sup>	Thickness, $\mu$ m	Apparent Density, g/cc	Dry Strength Properties								
					Breaking Length, km		TEA, kgm/m <sup>2</sup>		Et, kg/cm		Stretch, %		
					Av.	SD	Av.	SD	Av.	SD	Av.	SD	
Whole Pulp													
61	Blank controls	63.7	184	0.346	3.24	0.106	2.43	0.301	222	22.50	1.85	0.142	
62	PAE, 1.0	64.9	189	0.342	3.97	0.495	2.07	0.820	197	9.70	1.65	0.446	
63	PAE, 1.5	65.5	202	0.324	3.22	0.106	2.80	0.199	202	7.90	2.07	0.095	
64	PAE, 1.0; CMC, 0.4	63.4	184	0.344	3.88	0.070	3.12	0.350	218	13.60	2.06	0.146	
65	PAE, 1.0; PAA, 0.2	62.8	188	0.334	3.41	0.137	2.55	0.347	194	15.20	2.01	0.250	
Classified Pulp													
66	Blank controls	62.5	264	0.236	1.28	0.062	0.69	0.101	97.7	4.87	1.38	0.105	
67	PAE, 1.0	63.0	266	0.237	2.05	0.072	1.48	0.121	105	17.60	1.90	0.107	
68	PAE, 1.5	62.6	262	0.239	2.00	0.154	1.33	0.232	132	9.90	1.62	0.100	
69	PAE, 1.0; CMC, 0.4	63.2	247	0.256	3.39	0.082	3.02	0.176	169	6.60	2.38	0.143	
70	PAE, 1.0; PAA, 0.2 <sup>a</sup>	62.9	253	0.247	2.41	0.057	1.63	0.076	155	11.10	1.78	0.137	
Set No.	Additives, % based on fiber	Moisture Content, %	Moist Strength Properties								Wet		
			Breaking Length, km		TEA, kgm/m <sup>2</sup>		Et, kg/cm		Stretch, %		Moist Tensile Factor	Breaking Length, km	
			Av.	SD	Av.	SD	Av.	SD	Av.	SD		Av.	SD
Whole Pulp													
61	Blank controls	17.5	1.76	0.182	2.36	0.248	111.0	5.98	3.10	0.200	1.00	0.103	0.004
62	PAE, 1.0	17.5	2.08	0.177	3.58	0.475	80.7	5.29	4.02	0.288	1.18	1.330	0.035
63	PAE, 1.5	17.3	1.85	0.284	2.96	0.863	80.7	4.76	4.00	0.737	1.05	1.500	0.047
64	PAE, 1.0; CMC, 0.4	17.0	2.79	0.116	4.44	0.328	124.0	48.20	4.08	0.144	1.59	1.570	0.103
65	PAE, 1.0; PAA, 0.2	16.9	2.54	0.288	3.22	0.381	97.0	11.20	3.60	0.200	1.44	1.490	0.073
Classified Pulp													
66	Blank controls	--	0.64	0.057	0.51	0.039	45.0	2.17	2.11	0.214	1.00	0.050	0.004
67	PAE, 1.0	--	1.50	0.076	1.78	0.126	60.0	4.00	2.96	0.088	2.01	0.796	0.046
68	PAE, 1.5	--	1.25	0.111	1.20	0.263	55.3	3.86	2.66	0.291	1.93	0.730	0.034
69	PAE, 1.0; CMC, 0.4	--	2.36	0.249	3.33	0.652	85.2	9.10	3.74	0.317	3.64	1.500	0.054
70	PAE, 1.0; PAA, 0.2 <sup>a</sup>	--	1.47	0.047	1.81	0.076	61.1	13.30	3.03	0.092	2.27	0.846	0.046
Set No.	Additives, % based on fiber	Wet Tensile Factor	Dry STFI Compressive Strength, lb f/inch		Moist STFI Compressive Strength, lb f/inch		Moist Compressive Strength Factor						
			Whole Pulp		Classified Pulp		Classified Pulp						
			Av.	SD	Av.	SD	Av.	SD					
Whole Pulp													
61	Blank controls	1.00	6.70	3.62	1.00								
62	PAE, 1.0	12.91	--	--	--								
63	PAE, 1.5	14.56	7.29	3.98	1.1								
64	PAE, 1.0; CMC, 0.4	15.24	8.33	3.7	1.02								
65	PAE, 1.0; PAA, 0.2	14.47	7.60	3.5	0.79								
Classified Pulp													
66	Blank controls	1.00	--	--	--								
67	PAE, 1.0	15.90	--	--	--								
68	PAE, 1.50	14.60	--	--	--								
69	PAE, 1.0; CMC, 0.4	30.00	--	--	--								
70	PAE, 1.0; PAA, 0.2 <sup>a</sup>	16.90	--	--	--								

<sup>a</sup>Average of two sets of determinations.

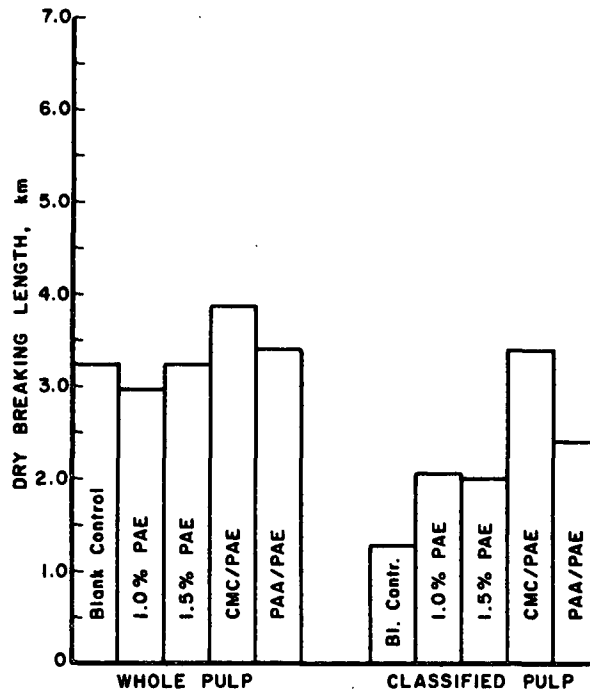


Figure 19. Dry breaking length - softwood TMP.

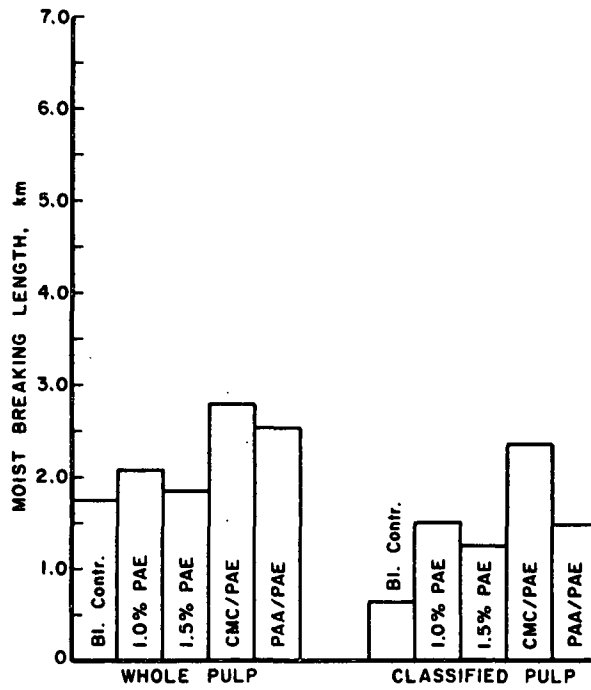


Figure 20. Moist breaking length - softwood TMP.

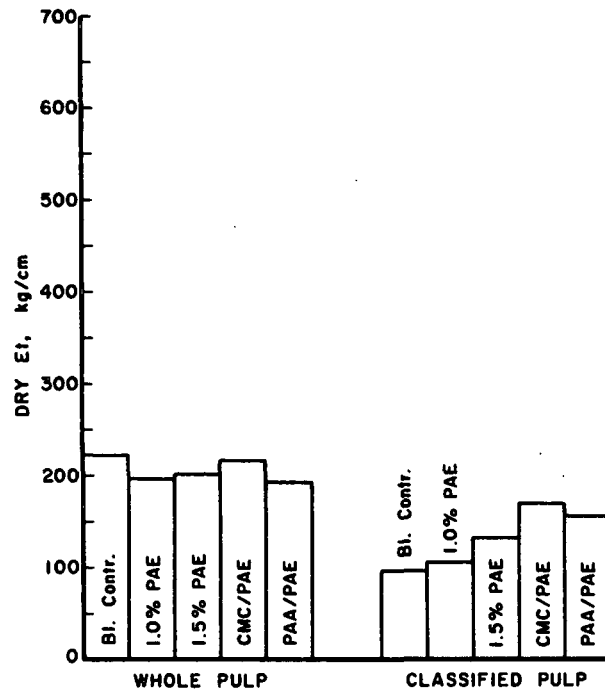


Figure 21. Dry Et - softwood TMP.

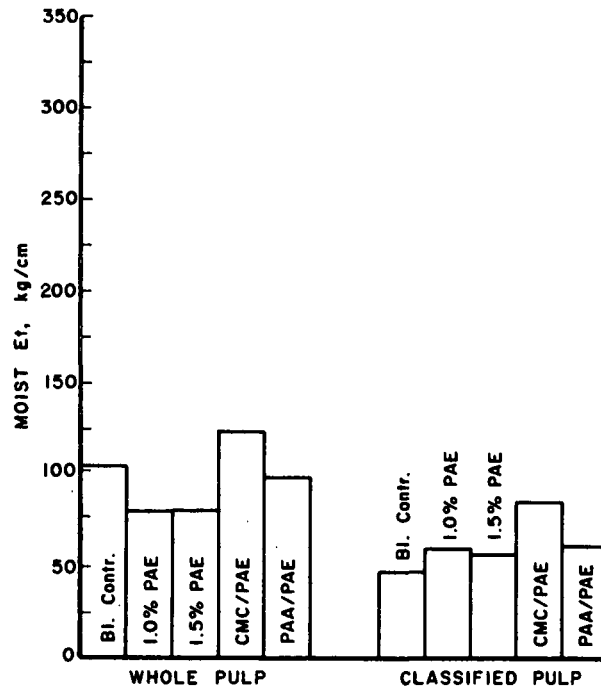


Figure 22. Moist Et - softwood TMP.

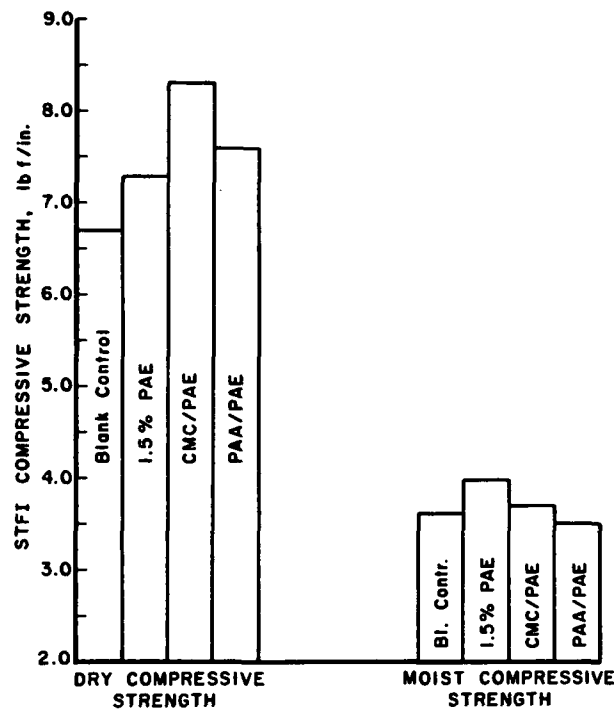


Figure 23. STFI compressive strength - whole softwood TMP.

#### THE EFFECT OF FINES AND FINES-POLYMER INTERACTIONS

Unit 3 examines the effect of fines and chemical bonding agents in two pulps differing widely in pulping procedure and wood source. In the first of these, a western hemlock TMP (Pulp No. 5) was beaten lightly to remove fiber bundles. Part of this pulp was classified on the Institute's continuous web former. Bauer-McNett classification of the whole pulp indicated a fines content of 30% (through 200 mesh sieve). Handsheets were subsequently formed from the whole and classified pulps and from the classified pulp after addition of 5, 10, 20, 30, and 60% of isolated fines. The effects of the duopolymer "standards" (CMC/PAE & PAA/PAE) on strength properties was determined by adding the bonding agents to

- a) the fines fraction only
- b) the classified fiber only, and
- c) both the classified and fines fractions in proportion to their weight.

Table 7. The effectiveness of bonding agents in a softwood unbleached kraft pulp. (49% yield).

Set No.	Additives, % based on fiber	Basis Wt., g/m <sup>2</sup>	Apparent Density, g/cc	Dry Strength Properties							
				Breaking Length, km		TEA, kgm/m <sup>2</sup>		Et, kg/cm		Stretch, %	
				Av.	SD	Av.	SD	Av.	SD	Av.	SD
Whole (Unclassified) Pulp											
71	Blank control	65.2	0.449	6.14	0.162	8.74	0.82	404	19.4	3.2	0.235
72	PAE, 1.0	61.9	0.453	7.06	0.643	9.86	2.36	380	12.5	3.4	0.537
73	PAE, 1.5	65.9	0.464	7.99	0.383	11.7	0.53	453	20.4	3.4	0.047
74	PAE, 1.0; CMC, 0.4	63.0	0.472	8.33	0.337	2.0	0.84	454	47.4	3.6	0.297
75	PAE, 1.0; PAA, 0.2	68.9	0.468	7.57	0.920	11.6	2.24	410	19.4	3.4	0.277
Classified Pulp											
24	Blank control	63.1	0.399	3.93	0.212	4.37	0.282	279	14.7	2.58	0.052
25	PAE, 1.0	67.3	0.387	5.73	0.279	6.92	0.847	450	16.9	2.76	0.241
26	PAE, 1.5	71.7	0.433	6.12	0.794	8.99	1.166	412	58.4	3.13	0.216
27	PAE, 1.0; CMC, 0.4	63.9	0.419	7.79	0.372	11.2	1.19	355	16.0	3.58	0.232
28	PAE, 1.0; PAA, 0.2	71.9	0.430	6.48	0.109	9.05	0.815	379	50.5	3.00	0.249
Set No.	Additives, % based on fiber	Moisture Content, %	Moist Strength Properties								
			Breaking Length, km		TEA, kgm/m <sup>2</sup>		Et, kg/cm		Stretch, %		Moist Tensile Factor
			Av.	SD	Av.	SD	Av.	SD	Av.	SD	
Whole (Unclassified) Pulp											
71	Blank control	15.8	4.30	0.165	8.73	0.972	200	10.8	4.5	0.330	1.00
72	PAE, 1.0	16.1	5.74	0.254	12.6	0.42	167	8.7	5.8	0.137	1.33
73	PAE, 1.5	16.1	6.55	0.433	15.6	1.11	208	17.0	5.3	0.232	1.52
74	PAE, 1.0; CMC, 0.4	15.9	6.76	0.178	15.5	0.38	194	9.8	5.4	0.072	1.57
75	PAE, 1.0; PAA, 0.2	16.0	6.70	0.159	16.2	2.03	210	10.8	5.5	0.425	1.56
Classified Pulp											
24	Blank control	--	1.98	0.114	2.68	0.186	109	6.9	3.39	0.073	1.00
25	PAE, 1.0	--	3.37	0.359	5.99	0.627	148	11.6	4.32	0.277	1.70
26	PAE, 1.5	--	3.79	0.327	6.65	0.492	131	11.2	4.59	0.121	2.00
27	PAE, 1.0; CMC, 0.4	--	4.86	0.311	9.05	1.076	150	3.4	5.16	0.253	2.45
28	PAE, 1.0; PAA, 0.2	--	4.05	0.331	7.51	0.96	172	21.4	4.41	0.206	2.05

Table 7 (Continued). The effectiveness of bonding agents in a softwood unbleached kraft pulp. (49% yield).

Set No.	Additives, % based on fiber	Wet Breaking Length, km		Wet Tensile Factor	Dry Compressive Strength, lb f/inch		Moist Compressive Strength, lb f/inch		Moist Compressive Strength Factor
		Av.	SD		Av.	SD	Av.	SD	
Whole (Unclassified) Pulp									
71	Blank control	0.200	0.020	1.0	7.74	0.648	4.17	0.300	1.00
72	PAE, 1.0	2.34	0.099	11.7	--	--	--	--	--
73	PAE, 1.5	2.76	0.144	13.8	10.46	0.806	5.10	0.505	1.22
74	PAE, 1.0; CMC, 0.4	2.50	0.203	12.5	9.43	0.894	4.69	0.386	1.13
75	PAE, 1.0; PAA, 0.2	2.44	0.208	12.2	10.59	0.670	4.50	0.769	1.08
Classified Pulp									
24	Blank control	0.158	0.012	1.0	6.32	0.47	3.22	0.457	1.00
25	PAE, 1.0	1.69	0.044	10.7	8.11	1.17	4.05	0.516	1.26
26	PAE, 1.5	1.92	0.119	12.1	9.06	0.76	4.27	0.408	1.33
27	PAE, 1.0; CMC, 0.4	2.27	0.200	14.4	11.31	1.18	4.84	0.515	1.50
28	PAE, 1.0; PAA, 0.2	1.81	0.062	11.4	10.48	0.93	4.76	0.483	1.48

Notes: Handsheets formed at pH 7-9.

The STFI compressive strengths were determined after the handsheets had aged approximately 1 year at room temperature.

Table 8. A comparison of duopolymer systems under acidic and slightly alkaline forming conditions. (49% yield southern pine unbleached kraft; whole pulp).

Set No.	Additives, % based on fiber	pH in Sheetmold	Basis Wt., g/m <sup>2</sup>	Apparent Density, g/cc	Dry Strength Properties							
					Breaking Length, km		TEA, kgm/m <sup>2</sup>		Et, kg/cm		Stretch, %	
					Av.	SD	Av.	SD	Av.	SD	Av.	SD
71	Blank controls	7-9	65.2	0.449	6.14	0.162	8.74	0.824	404	19.4	3.2	0.235
72	PAE, 1.0	7-9	61.9	0.453	7.06	0.643	9.89	2.36	380	12.5	3.4	0.537
73	PAE, 1.5	7-9	65.9	0.464	7.99	0.383	11.7	0.53	453	20.4	3.4	0.047
74	PAE, 1.0; CMC, 0.4	7-9	63.0	0.472	8.33	0.337	12.0	0.84	454	47.4	3.6	0.297
75	PAE, 1.0; PAA, 0.2	7-9	68.9	0.468	7.57	0.920	11.6	2.24	410	19.4	3.4	0.277
76	PAE, 1.0	4.5	64.7	0.455	6.60	0.353	9.33	0.958	415	16.6	3.3	0.26
77	PAE, 1.5	4.5	69.1	0.472	7.25	0.266	11.3	1.01	474	19.4	3.4	0.20
78	PAE, 1.0; CMC, 0.4	4.5	68.5	0.478	7.63	0.260	11.8	0.83	492	14.3	3.4	0.19
79	PAE, 1.0; PAA, 0.2	4.5	66.6	0.494	7.78	0.352	12.9	1.48	483	22.3	3.7	0.34

Set No.	Additives, % based on fiber	Moisture Content, %	Moist Strength Properties								
			Breaking Length, km		TEA, kgm/m <sup>2</sup>		Et, kg/cm		Stretch, %		Moist Tensile Factor
			Av.	SD	Av.	SD	Av.	SD	Av.	SD	
71	Blank control	15.8	4.30	0.165	8.73	0.972	200	10.8	4.5	0.330	1.0
72	PAE, 1.0	16.1	5.74	0.254	12.6	0.42	167	8.7	5.8	0.137	1.33
73	PAE, 1.5	16.1	6.55	0.433	15.6	1.11	208	17.0	5.3	0.232	1.52
74	PAE, 1.0; CMC, 0.4	15.9	6.76	0.178	15.5	0.38	194	9.8	5.4	0.072	1.57
75	PAE, 1.0; PAA, 0.2	16.0	6.70	0.159	16.2	2.03	210	10.8	5.5	0.425	1.56
76	PAE, 1.0	15.2	3.88	0.269	7.30	1.20	180	11.9	5.3	0.41	0.90
77	PAE, 1.5	15.0	5.50	0.103	13.0	1.59	200	6.7	5.3	0.15	1.28
78	PAE, 1.0; CMC, 0.4	15.1	5.90	0.268	13.8	0.88	207	14.4	5.7	0.14	1.37
79	PAE, 1.0; PAA, 0.2	15.5	5.46	0.221	13.1	1.41	179	8.5	5.9	0.37	1.27

Table 8 (Continued). A comparison of duopolymer systems under acidic and slightly alkaline forming conditions. (49% yield southern pine unbleached kraft; whole pulp).

Set No.	Additives, % based on fiber	Wet Breaking Length, km		Wet Tensile Factor	Dry Compressive Strength, lb f/inch		Moist Compressive Strength, lb f/inch		Moist Compressive Strength Factor
		Av.	SD		Av.	SD	Av.	SD	
71	Blank control	0.200	0.020	1.0	7.74	0.648	4.16	0.300	1.00
72	PAE, 1.0	2.34	0.099	11.7	--	--	--	--	--
73	PAE, 1.5	2.76	0.144	13.8	10.46	0.806	5.09	0.504	1.22
74	PAE, 1.0; CMC, 0.4	2.50	0.203	12.5	9.43	0.893	4.69	0.385	1.13
75	PAE, 1.0; PAA, 0.2	2.44	0.208	12.2	10.59	1.060	4.50	0.370	1.08
76	PAE, 1.0	2.12	0.161	10.6	7.30	0.525	4.01	0.262	0.96
77	PAE, 1.5	2.49	0.130	12.5	10.55	0.984	4.95	0.464	1.19
78	PAE, 1.0; CMC, 0.4	2.44	0.112	12.2	11.57	1.00	4.18	0.349	1.00
79	PAE, 1.0; PAA, 0.2	2.34	0.044	11.7	11.08	0.750	4.82	0.623	1.16

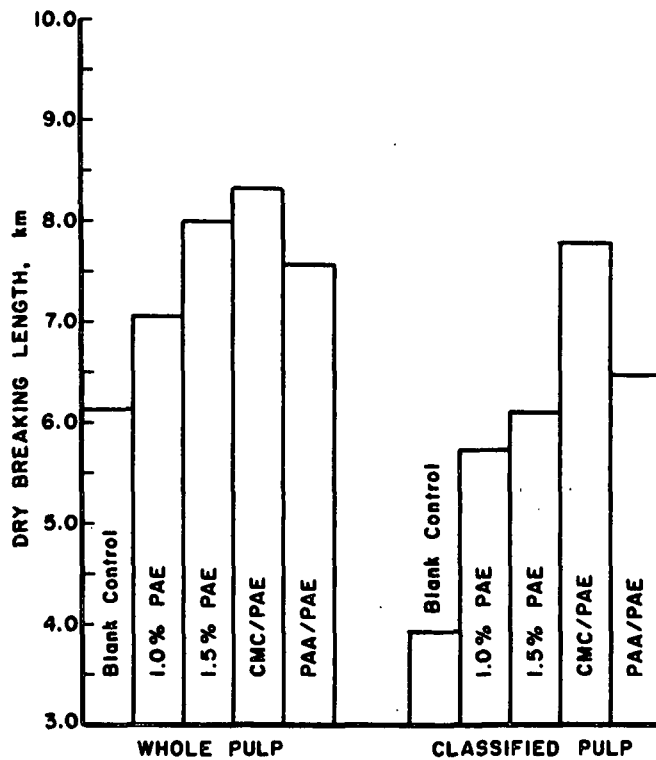


Figure 24. Dry breaking length - 49% yield softwood unbl. kraft.

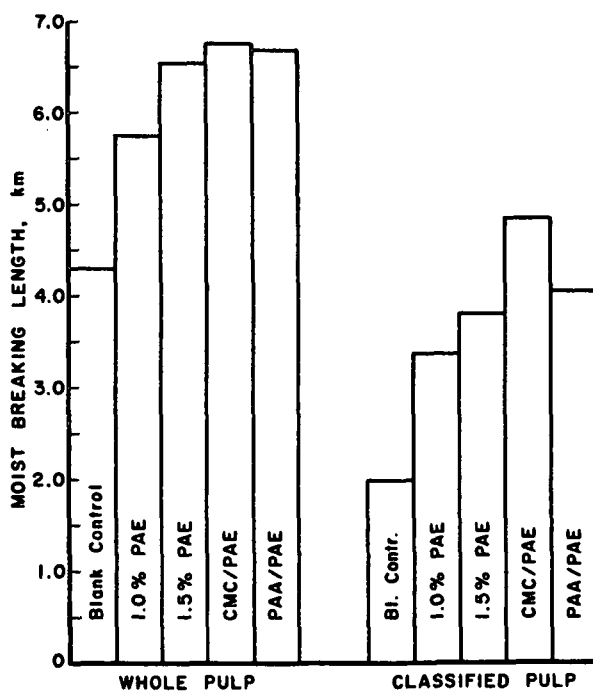


Figure 25. Moist breaking length - 49% softwood unbl. kraft.

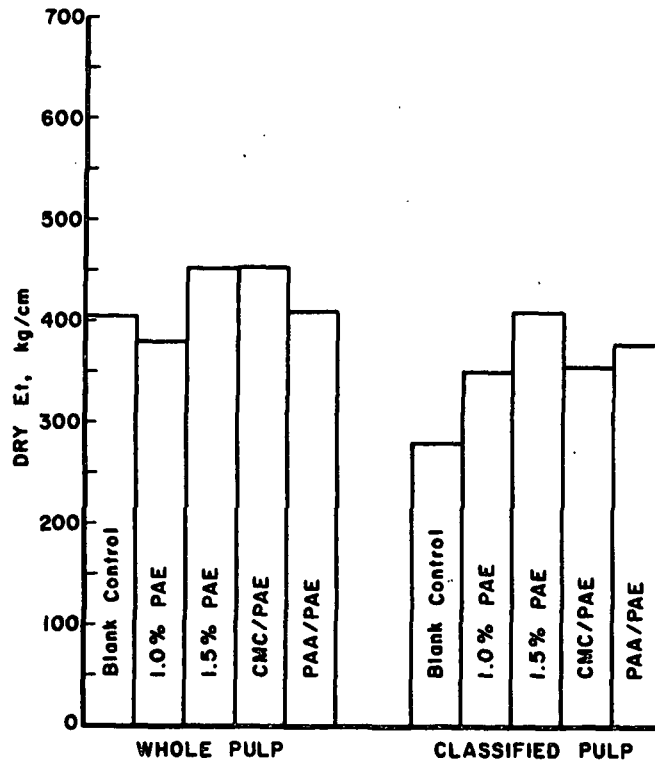


Figure 26. Dry Et - 49% yield softwood unbl. kraft.

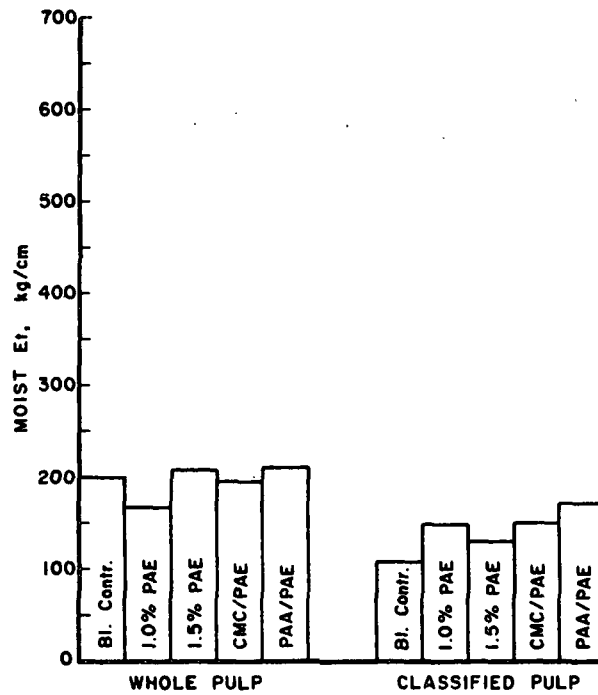


Figure 27. Moist Et - 49% yield softwood unbl. kraft.

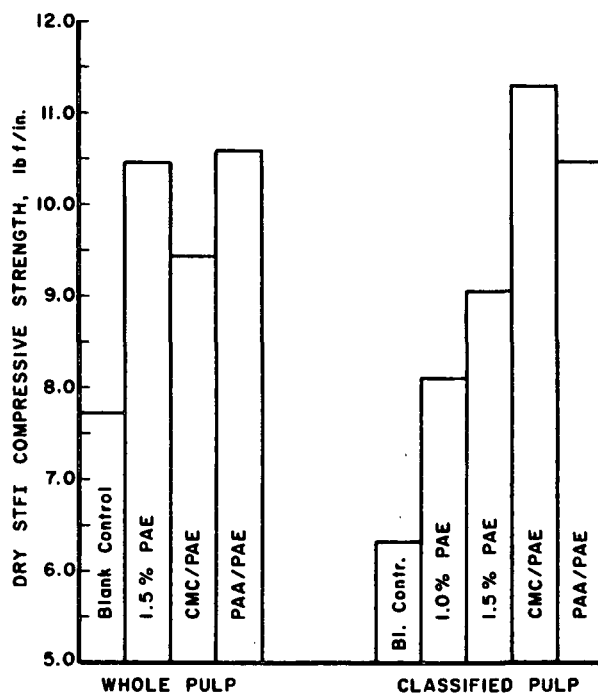


Figure 28. Dry STFI compressive strength - 49% yield softwood unbl. kraft.

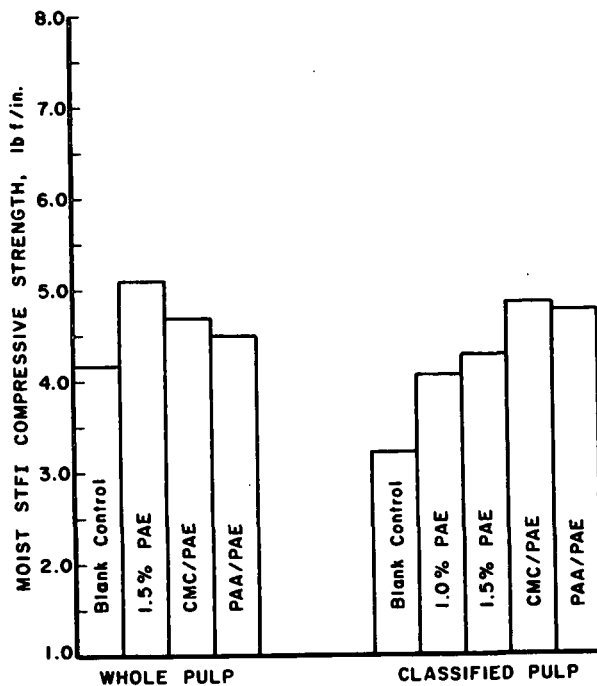


Figure 29. Moist STFI compressive strength - 49% yield softwood unbl. kraft.

Table 9. The effectiveness of bonding agents in a softwood unbleached kraft pulp (46.5-47.0% yield).

Set No.	Additives, % based on fiber	Basis Wt., g/m <sup>2</sup>	Apparent Density, g/cc	Dry Strength Properties							
				Breaking Length, km		TEA, kgm/m <sup>2</sup>		Et, kg/cm		Stretch, %	
				Av.	SD	Av.	SD	Av.	SD	Av.	SD
Whole (Unclassified) Pulp											
80	Blank control	63.9	0.484	5.20	0.196	7.93	0.939	385	6.4	3.3	0.25
81	PAE, 1.0	64.7	0.494	6.14	0.322	8.83	1.354	412	10.9	3.2	0.34
82	PAE, 1.5	62.8	0.485	6.31	0.268	9.47	0.757	395	16.0	3.5	0.22
83	PAE, 1.0; CMC, 0.4	61.8	0.501	7.35	0.085	13.05	0.745	397	15.3	4.3	0.24
84	PAE, 1.0; PAA, 0.2	61.2	0.506	6.97	0.280	11.0	1.09	410	6.7	3.8	0.24
Classified Pulp											
47	Blank control	62.9	0.447	3.83	0.284	4.51	0.563	316	33.5	2.6	0.26
48	PAE, 1.0	65.8	0.442	5.27	0.361	7.46	0.954	357	26.6	3.2	0.21
49	PAE, 1.5	61.4	0.447	5.38	0.368	7.64	1.236	313	5.7	3.5	0.36
50	PAE, 1.0; CMC, 0.4	64.9	0.484	7.27	0.531	12.2	1.41	409	22.2	4.0	0.22
51	PAE, 1.0; PAA, 0.2	64.7	0.466	6.14	0.380	10.4	1.01	368	24.9	3.9	0.27
Set No.	Additives % based on fiber	Moisture Content, % (at 91-93% RH)	Moist Strength Properties								Moist Tensile Factor
			Breaking Length, km		TEA, kgm/m <sup>2</sup>		Et, kg/cm		Stretch, %		
			Av.	SD	Av.	SD	Av.	SD	Av.	SD	
Whole (unclassified) pulp											
80	Blank control	15.3	2.84	0.224	5.52	0.706	141	4.7	4.7	0.37	1.00
81	PAE, 1.0	15.9	4.42	0.277	9.76	1.33	135	7.4	6.0	0.39	1.50
82	PAE, 1.5	15.4	4.48	0.188	8.95	0.429	132	8.6	5.8	0.20	1.58
83	PAE, 1.0; CMC, 0.4	15.3	5.17	0.244	11.39	0.851	140	3.3	6.4	0.20	1.82
84	PAE, 1.0; PAA, 0.2	15.8	4.60	0.152	9.77	0.763	135	11.0	6.2	0.28	1.62
Classified pulp											
47	Blank control	15.9	1.88	0.082	3.09	0.354	111	9.3	3.9	0.40	1.00
48	PAE, 1.0	15.2	3.64	0.336	7.74	1.03	129	5.1	5.1	0.35	1.94
49	PAE, 1.5	14.8	3.73	0.199	7.54	0.557	120	7.6	5.3	0.28	1.98
50	PAE, 1.0; CMC, 0.4	15.5	4.78	0.458	11.92	1.05	142	5.5	6.2	0.28	2.54
51	PAE, 1.0; PAA, 0.2	15.5	4.17	0.264	9.21	0.718	125	11.9	5.8	0.30	2.22

Table 9 (Continued). The effectiveness of bonding agents in a softwood unbleached kraft pulp (46.5-47.0% yield).

Set No.	Additives % based on fiber	Wet Breaking Length, km		Wet Tensile Factor	Dry STFI Compressive Strength, lb f/inch		Moist STFI Compressive Strength, lb f/inch		Moist Compressive Strength Factor
		Av.	SD		Av.	SD	Av.	SD	
Whole Pulp									
80	Blank control	0.191	0.010	1.0	8.92	0.707	3.97	0.352	1.00
81	PAE, 1.0	1.81	0.137	9.5	10.56	1.279	--	--	--
82	PAE, 1.5	2.13	0.197	11.1	10.54	1.061	4.41	0.484	1.11
83	PAE, 1.0; CMC, 0.4	2.19	0.090	11.5	10.07	0.544	4.37	0.302	1.10
84	PAE, 1.0; PAA, 0.2	1.91	0.070	10.0	10.11	0.875	3.78	0.454	0.95
Classified Pulp									
47	Blank control	0.129	0.008	1.0	7.13	0.777	2.89	0.208	1.00
48	PAE, 1.0	1.27	0.152	9.8	8.79	0.872	3.01	0.490	1.04
49	PAE, 1.5	1.66	0.095	12.9	8.36	0.777	3.02	0.291	1.04
50	PAE, 1.0; CMC, 0.4	2.30	0.138	17.8	10.12	0.813	3.75	0.326	1.30
51	PAE, 1.0; PAA, 0.2	1.73	0.112	13.4	8.97	0.641	3.41	0.388	1.18

Table 10. The effectiveness of bonding agents in a softwood chemimechanical pulp (85-88% yield).

Set No.	Additives, % based on fiber	Basis Wt., g/m <sup>2</sup>	Apparent Density, g/cc	Dry Strength Properties								
				Breaking Length, km		TEA, kgm/m <sup>2</sup>		Et, kg/cm		Stretch, %		
				Av.	SD	Av.	SD	Av.	SD	Av.	SD	
Whole (Unclassified) Pulp												
85	Blank controls	63.0	0.386	5.24	0.222	4.04	0.545	352	17.4	1.9	0.16	
86	PAE, 1.0	62.9	0.396	6.79	0.282	6.03	0.930	377	13.3	2.2	0.23	
87	PAE, 1.5	63.3	0.396	6.25	0.379	4.95	0.436	374	18.8	2.0	0.07	
88	PAE, 1.0; CMC, 0.4	63.2	0.405	6.86	0.424	6.14	0.612	397	16.7	2.2	0.14	
89	PAE, 1.0; PAA, 0.2	62.9	0.390	6.62	0.311	5.84	0.589	379	13.6	2.2	0.14	
Classified Pulp												
90	Blank controls	64.3	0.339	3.93	0.150	2.64	0.176	290	11.5	1.6	0.05	
91	PAE, 1.0	64.6	0.336	5.59	0.097	5.08	0.257	300	13.0	2.3	0.12	
92	PAE, 1.5	64.9	0.344	5.15	0.226	4.02	0.442	294	17.5	2.0	0.16	
93	PAE, 1.0; CMC, 0.4	61.9	0.352	6.33	0.424	5.86	0.909	318	9.9	2.4	0.20	
94	PAE, 1.0; PAA, 0.2	65.0	0.357	6.08	0.127	5.53	0.448	340	18.0	2.2	0.15	
Set No.	Additives % based on fiber	Moisture, Content, % (at 91-93% RH)	Moist Strength Properties								Moist Tensile Factor	
			Breaking Length, km		TEA, kgm/m <sup>2</sup>		Et, kg/cm		Stretch, %			
			Av.	SD	Av.	SD	Av.	SD	Av.	SD		
Whole (Unclassified) Pulp												
85	Blank control	17.9		2.59	0.173	2.67	0.173	164	18.0	2.5	0.10	1.00
86	PAE, 1.0	18.6		4.25	0.324	5.97	0.712	148	11.0	3.8	0.33	1.64
87	PAE, 1.5	18.0		4.56	0.058	6.58	0.808	151	6.0	3.6	0.21	1.83
88	PAE, 1.0; CMC, 0.4	18.1		4.80	0.144	7.45	0.326	170	5.5	3.8	0.07	1.93
89	PAE, 1.0; PAA, 0.2	17.8		4.77	0.128	7.30	0.541	171	11.4	3.7	0.06	1.92
Classified Pulp												
90	Blank controls	18.2		1.70	0.091	1.28	0.187	131	5.3	1.8	0.14	1.00
91	PAE, 1.0	18.2		3.56	0.141	4.66	0.476	125	5.0	3.5	0.24	2.09
92	PAE, 1.5	17.7		3.80	0.156	4.68	0.476	130	6.4	3.4	0.23	2.23
93	PAE, 1.0; CMC, 0.4	18.0		4.06	0.415	5.21	0.698	122	9.3	3.8	0.20	2.39
94	PAE, 1.0; PAA, 0.2	18.1		3.92	0.340	5.24	0.755	135	6.5	3.6	0.25	2.31

Table 10 (Continued). The effectiveness of bonding agents in a softwood chemimechanical pulp (85-88% yield).

Set No.	Additives % based on fiber	Wet Breaking Length, km		Wet Tensile Factor	Dry STFI Compressive Strength, lb f/inch		Moist STFI Compressive Strength, lb f/inch		Moist Compressive Strength Factor
		Av.	SD		Av.	SD	Av.	SD	
Whole (Unclassified) Pulp									
85	Blank control	0.143	0.012	1.00	8.54	0.622	4.14	0.391	1.00
86	PAE, 1.0	2.15	0.105	15.0	9.83	0.725	4.51	0.594	1.09
87	PAE, 1.5	2.25	0.086	15.7	10.31	0.545	5.03	0.527	1.21
88	PAE, 1.0; CMC, 0.4	2.28	0.074	15.9	9.73	0.500	5.11	0.419	1.23
89	PAE, 1.0; PAA, 0.2	2.20	0.075	15.4	10.6	0.933	4.48	0.329	1.08
Classified Pulp									
90	Blank controls	0.073	0.013	1.00	6.20	0.463	2.83	0.309	1.00
91	PAE, 1.0	1.52	0.087	20.8	7.77	0.665	3.48	0.411	1.23
92	PAE, 1.5	1.72	0.051	23.6	8.05	0.732	3.34	0.420	1.18
93	PAE, 1.0; CMC, 0.4	1.94	0.110	26.6	8.03	0.759	3.54	0.439	1.25
94	PAE, 1.0; PAA, 0.2	1.88	0.116	25.8	8.76	0.797	3.54	0.270	1.25

Table 11. The effectiveness of polymer combinations in softwood bleached kraft.

Set No.	Additives, % based on fiber	Basis Wt., g/m <sup>2</sup>	Apparent Density, g/cc	Dry Strength Properties							
				Breaking Length, km		TEA, kgm/m <sup>2</sup>		Et, kg/cm		Stretch, %	
				Av.	SD	Av.	SD	Av.	SD	Av.	SD
Whole Pulp											
95	Blank control	65.2	0.516	4.35	0.220	6.49	0.806	340	12.4	3.2	0.25
96	PAE, 1.0	64.7	0.509	5.15	0.345	8.63	0.898	341	14.5	3.7	0.17
97	PAE, 1.5	64.7	0.520	5.53	0.290	8.72	0.906	359	13.3	3.5	0.22
98	PAE, 1.0; CMC, 0.4	67.9	0.537	6.88	0.147	13.43	1.158	396	22.3	4.3	0.35
99	PAE, 1.0; PAA, 0.2	65.1	0.519	5.73	0.304	9.68	1.034	363	10.2	3.8	0.21
Classified Pulp											
100	Blank control	64.7	0.482	3.41	0.133	4.03	0.525	265	10.8	2.6	0.25
101	PAE, 1.0	65.6	0.485	4.66	0.247	7.61	0.511	307	16.4	3.6	0.09
102	PAE, 1.5	65.2	0.492	4.41	0.119	6.07	0.775	294	12.7	3.1	0.33
103	PAE, 1.0; CMC, 0.4	66.2	0.501	6.74	0.470	11.9	1.05	359	25.8	4.1	0.14
104	PAE, 1.0; PAA, 0.2	72.8	0.502	4.65	0.386	7.77	1.178	349	25.1	3.3	0.31
105	99:6:0.4 Bl. Kraft: CMC Fiber, PAE, 1.0	69.1	0.491	4.77	0.565	7.67	1.579	322	27.6	3.4	0.34
106	99:1 Bl. Kraft: CMC Fiber, PAE, 1.0	67.3	0.489	4.89	0.204	8.14	0.700	295	20.0	3.7	0.24
107	95:5 Bl. Kraft: CMC Fiber, PAE, 1.0	67.9	0.469	6.16	0.263	10.9	0.31	321	22.9	4.0	0.12
108	90:10 Bl. Kraft: CMC Fiber, PAE, 1.0	68.9	0.452	6.02	0.549	11.2	1.41	309	16.9	4.2	0.38

Table 11 (Continued). The effectiveness of polymer combinations in softwood bleached kraft.

Set No.	Additives % based on fiber	Moisture, Content, % (at 91-93% RH)	Moist Strength Properties								Moist Tensile Factor
			Breaking Length, km		TEA, kgm/m <sup>2</sup>		Et, kg/cm		Stretch, %		
			Av.	SD	Av.	SD	Av.	SD	Av.	SD	
Whole Pulp											
95	Blank control	13.6	2.44	0.122	4.65	0.672	149	7.0	4.3	0.47	1.0
96	PAE, 1.0	14.8	3.43	0.268	7.93	0.648	118	10.3	6.0	0.23	--
97	PAE, 1.5	14.0	3.73	0.341	7.64	1.308	137	6.4	5.4	0.45	1.53
98	PAE, 1.0; CMC, 0.4	14.0	4.91	0.144	11.5	1.01	157	8.8	6.1	0.31	2.01
99	PAE, 1.0; PAA, 0.2	13.3	3.80	0.176	8.50	0.479	145	13.9	5.7	0.17	1.56
Classified Pulp											
100	Blank control	13.9	1.73	0.134	2.27	0.370	129	12.3	3.2	0.24	1.00
101	PAE, 1.0	14.7	2.91	0.243	5.82	0.807	110	4.9	5.1	0.26	1.68
102	PAE, 1.5	13.8	3.04	0.094	5.01	0.398	128	7.6	4.6	0.17	1.76
103	PAE, 1.0; CMC, 0.4	13.6	4.81	0.218	9.48	0.876	148	9.0	5.7	0.20	2.78
104	PAE, 1.0; PAA, 0.2	14.2	2.83	0.111	5.54	0.551	144	4.8	4.7	0.24	1.64
105	99.6:0.4 Bl. Kraft: CMC Fiber, PAE, 1.0	14.1	3.15	0.289	5.59	0.757	130	9.9	4.7	0.25	1.82
106	99:1 Bl. Kraft: CMC Fiber, PAE, 1.0	13.5	3.47	0.221	6.85	0.994	133	8.5	5.0	0.41	2.00
107	95:5 Bl. Kraft: CMC Fiber, PAE, 1.0	14.6	4.02	0.257	9.19	0.432	120	11.9	6.0	0.30	2.32
108	90:10 Bl. Kraft: CMC Fiber, PAE, 1.0	15.3	3.79	0.213	8.05	0.631	120	6.0	5.6	0.25	2.19

Table 11 (Continued). The effectiveness of polymer combinations in softwood bleached kraft.

Set No.	Additives % based on fiber	Wet Breaking Length, km		Wet Tensile Factor	Bright-ness, <sup>a</sup> %	Dry STFI Compressive Strength, lb f/inch		Moist STFI Compressive Strength, lb f/inch		Moist Compressive Strength Factor
		Av.	SD			Av.	SD	Av.	SD	
Whole Pulp										
95	Blank control	0.109	0.033	1.00	82.2	7.84	0.311	3.03	0.193	1.00
96	PAE, 1.0	1.31	0.128	12.0	--	8.49	0.411	3.07	0.334	1.34
97	PAE, 1.5	1.36	0.091	12.48	72.8	8.66	0.406	3.06	0.226	1.01
98	PAE, 1.0; CMC, 0.4	1.97	0.039	18.07	75.2	9.69	0.508	3.31	0.114	1.09
99	PAE, 1.0; PAA, 0.2	1.16	0.054	10.64	79.8	8.59	0.488	3.33	0.180	1.10
Classified Pulp										
100	Blank control	0.100	0.013	1.00	84.5	6.22	0.320	2.92	0.274	1.00
101	PAE, 1.0	1.03	0.070	10.3	--	6.65	0.358	2.97	0.228	1.02
102	PAE, 1.5	1.01	0.023	10.1	77.8	6.96	0.439	3.04	0.190	1.04
103	PAE, 1.0; CMC, 0.4	1.92	0.038	19.2	75.3	8.30	0.482	3.49	0.165	1.19
104	PAE, 1.0; PAA, 0.2	0.805	0.046	8.05	80.0	7.99	0.523	3.59	0.251	1.23
105	99.6:0.4 Bl. Kraft: CMC Fiber, PAE, 1.0	1.10	0.154	11.0	78.3	7.66	0.718	3.34	0.348	1.14
106	99:1 Bl. Kraft: CMC Fiber, PAE, 1.0	1.20	0.052	12.0	79.1	7.58	0.525	3.23	0.180	1.11
107	95:5 Bl. Kraft: CMC Fiber, PAE, 1.0	1.67	0.136	16.7	74.3	8.25	0.782	3.26	0.203	1.12
108	90:10 Bl. Kraft: CMC Fiber, PAE, 1.0	1.46	0.107	14.6	77.0	8.36	0.704	3.12	0.225	1.07

Diffuse Reflective FTIR Analysis  
Absorbance Peaks Occurring at

Set No.	Additives, % based on fiber	1740		1650		A1740/A1650
		Ester		Amide		
Classified Pulp						
103	PAE, 1.0; CMC, 0.4	1.02		2.18		0.466
105	99.6:0.4 Bl. Kraft: CMC Fiber, PAE, 1.0	0.67		1.99		0.337

<sup>a</sup>Brightness was not measured immediately after handsheet preparation; hence values may be in error.

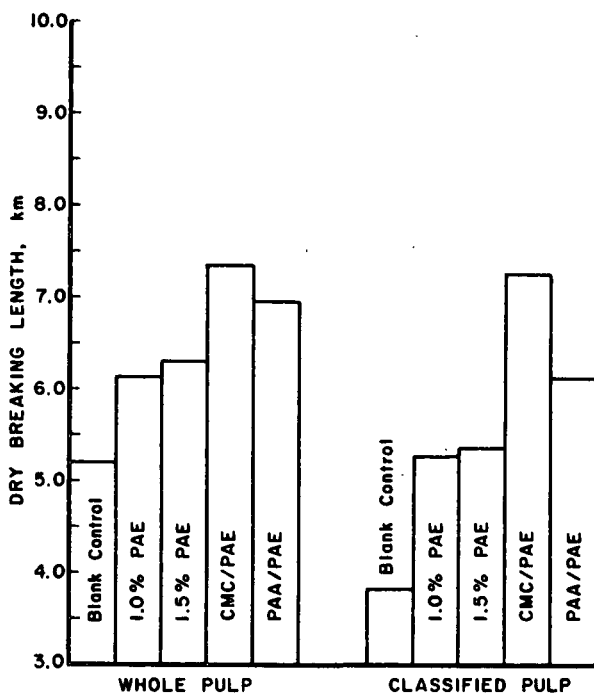


Figure 30. Dry breaking length - once dried softwood unbl. kraft (46-47% yield).

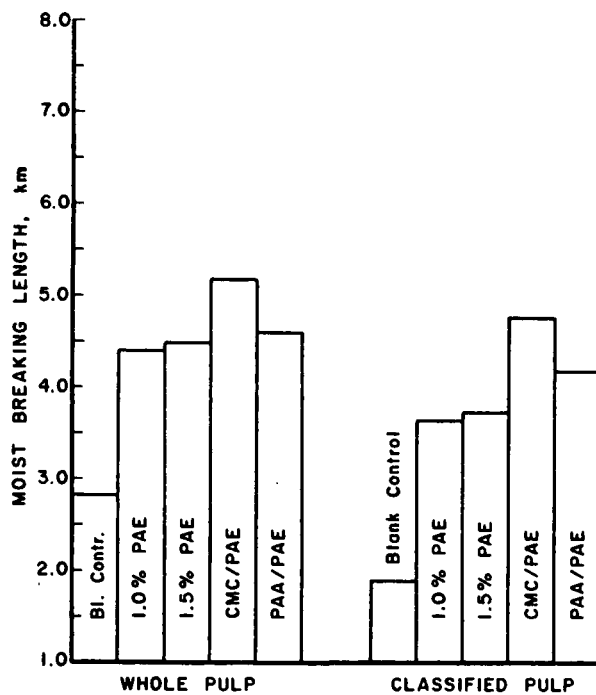


Figure 31. Moist breaking length - once dried softwood unbl. kraft (46-47% yield).

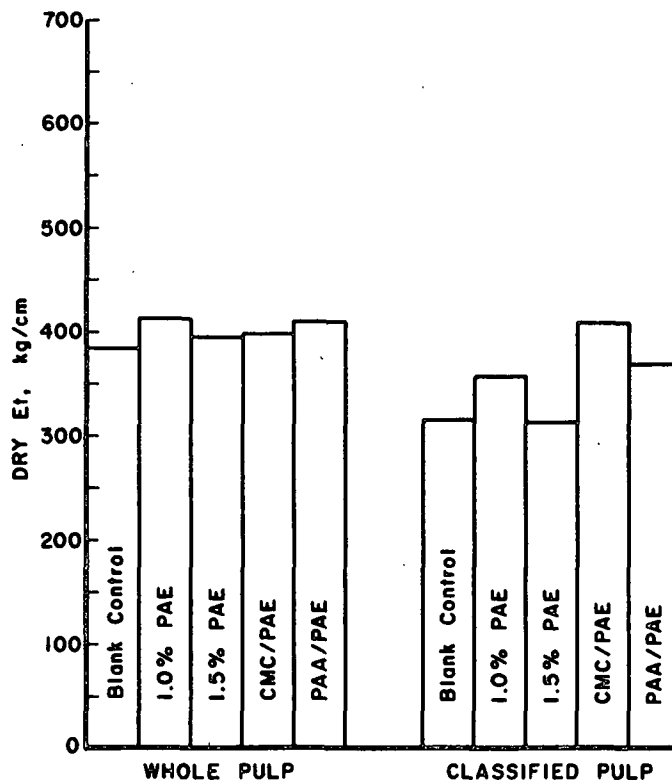


Figure 32. Dry Et - once dried softwood unbl. kraft (46-47% yield).

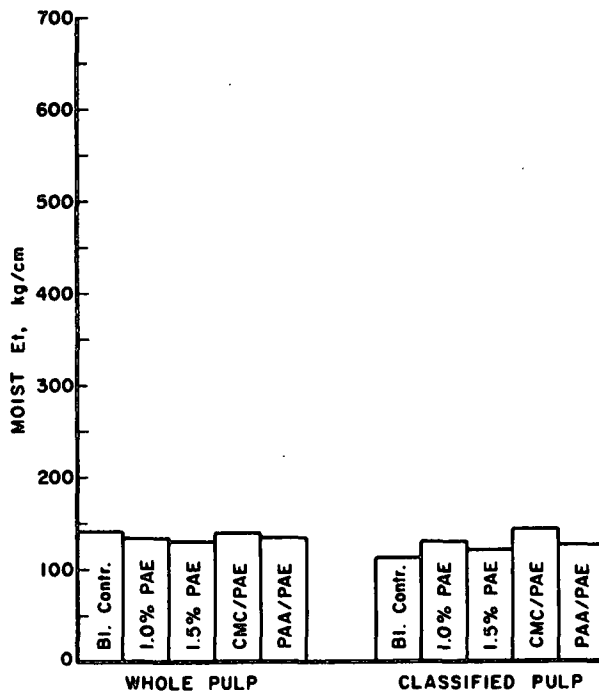


Figure 33. Moist Et - once dried softwood unbl. kraft (46-47% yield).

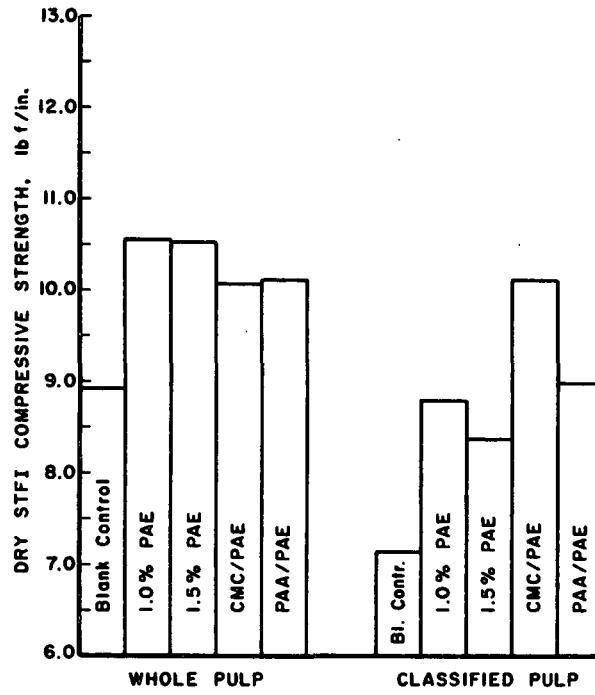


Figure 34. Dry STFI compressive strength - once dried softwood unbl. kraft.

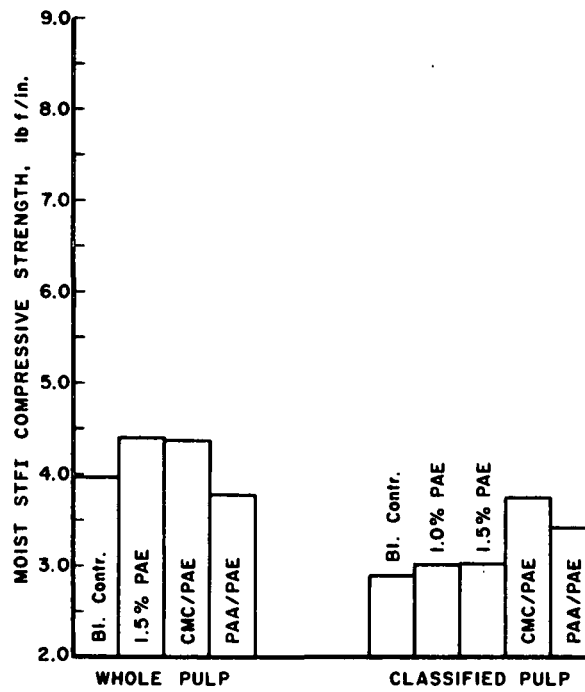


Figure 35. Moist STFI compressive strength - once dried softwood unbl. kraft.

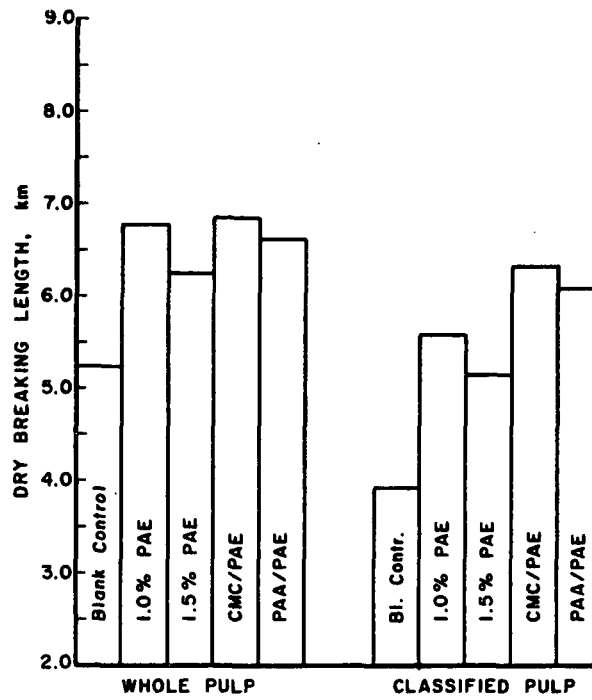


Figure 36. Dry breaking length - softwood chemimechanical pulp.

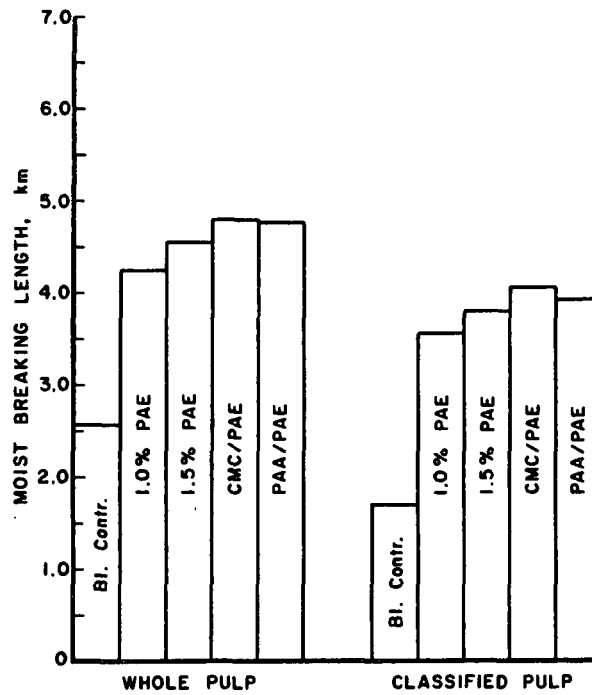


Figure 37. Moist breaking length - softwood chemimechanical pulp.

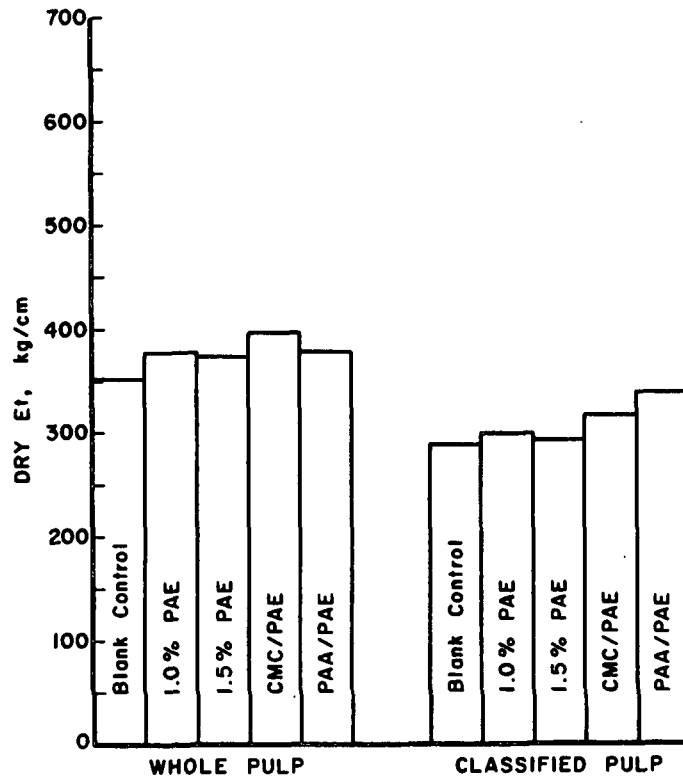


Figure 38. Dry Et - softwood chemimechanical pulp.

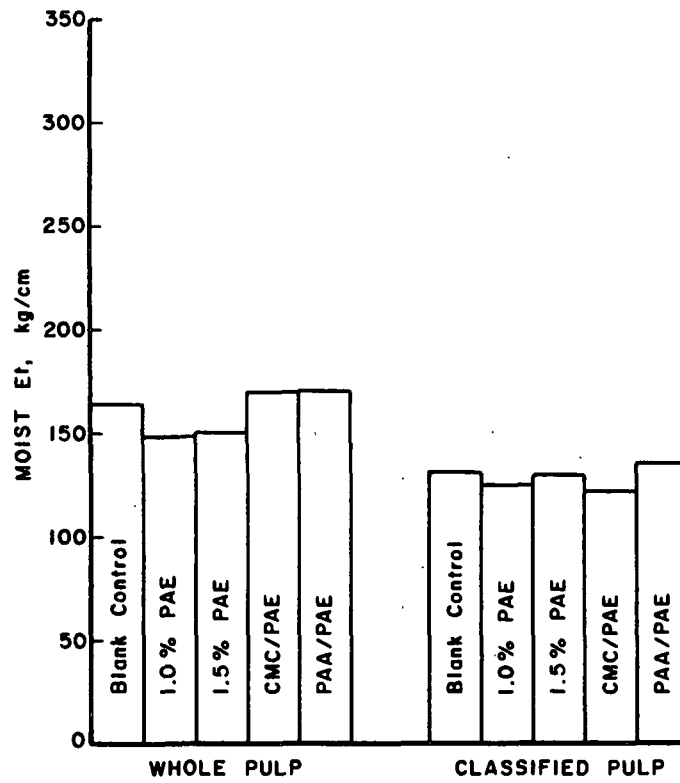


Figure 39. Moist Et - softwood chemimechanical pulp.

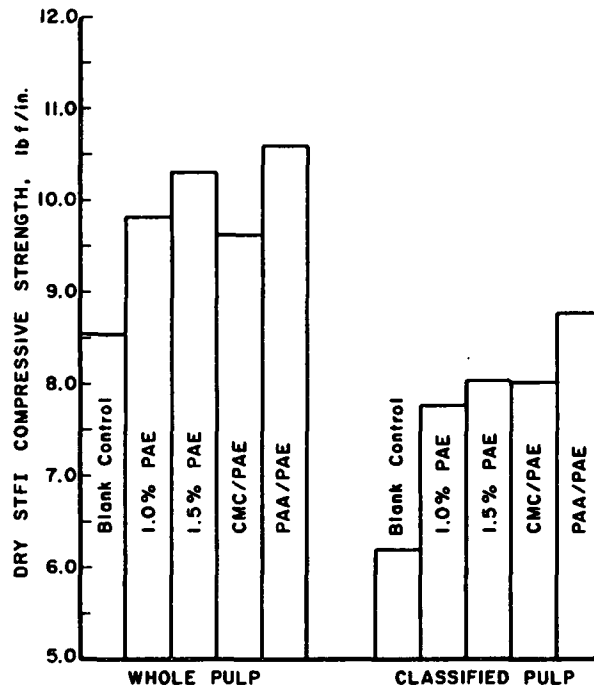


Figure 40. Dry STFI compressive strength - softwood chemimechanical pulp.

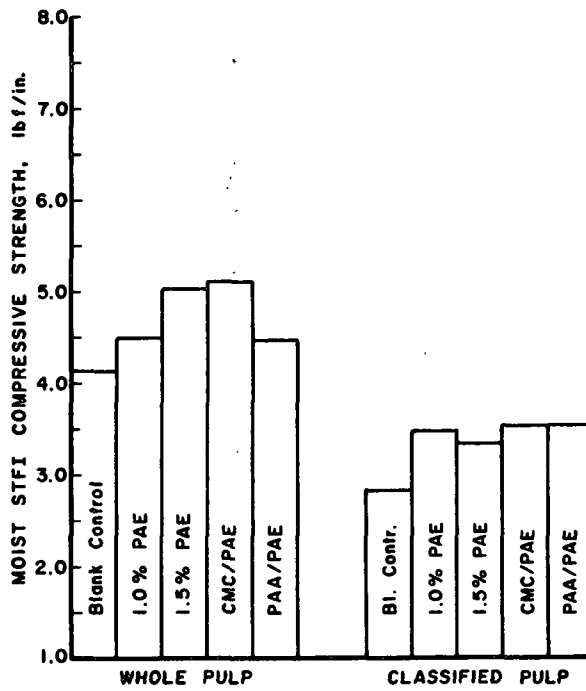


Figure 41. Moist STFI compressive strength - softwood chemimechanical pulp.

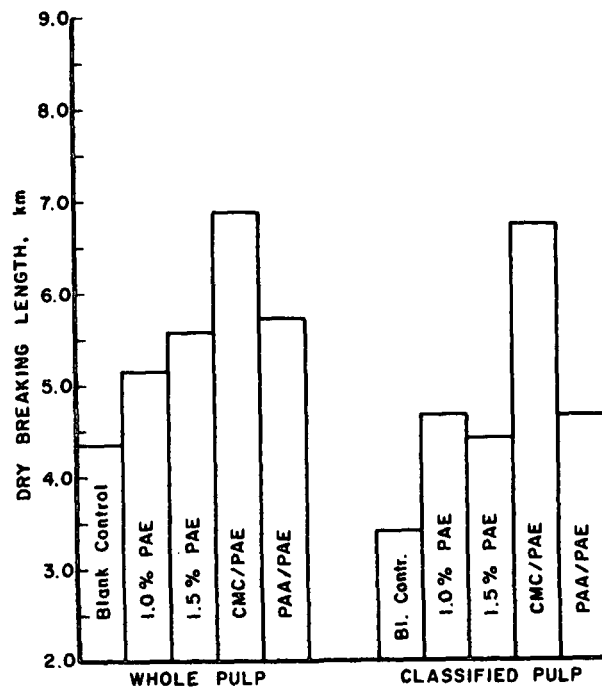


Figure 42. Dry breaking length - softwood bleached kraft.

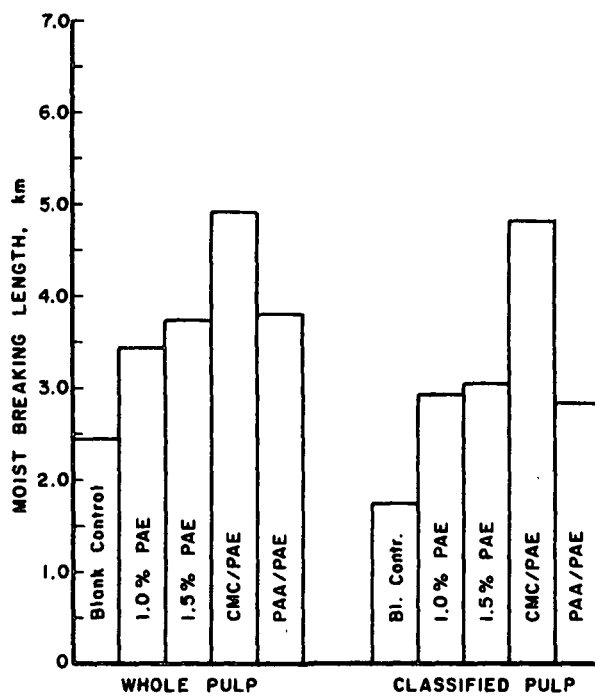


Figure 43. Moist breaking length - softwood bleached kraft.

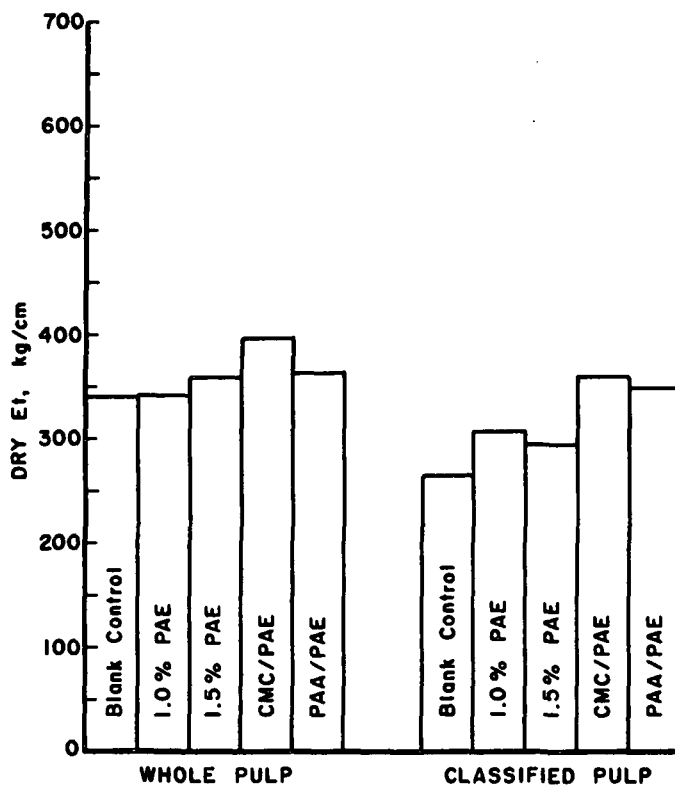


Figure 44. Dry Et - softwood bleached kraft.

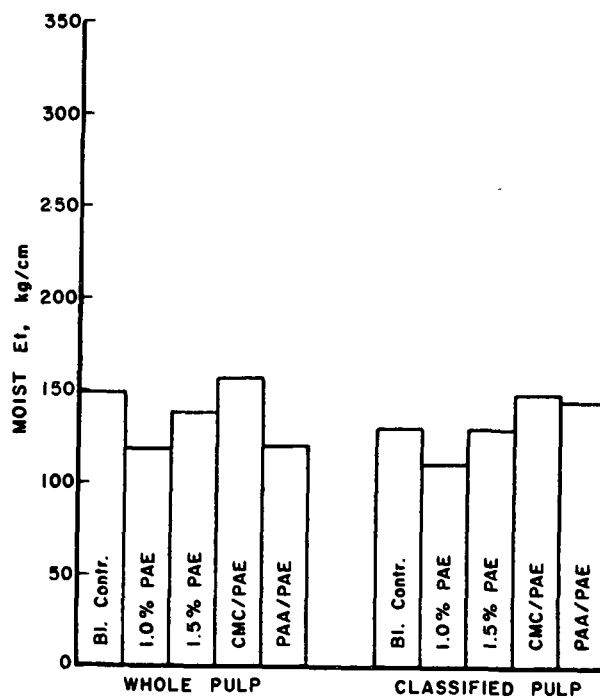


Figure 45. Moist Et - softwood bleached kraft.

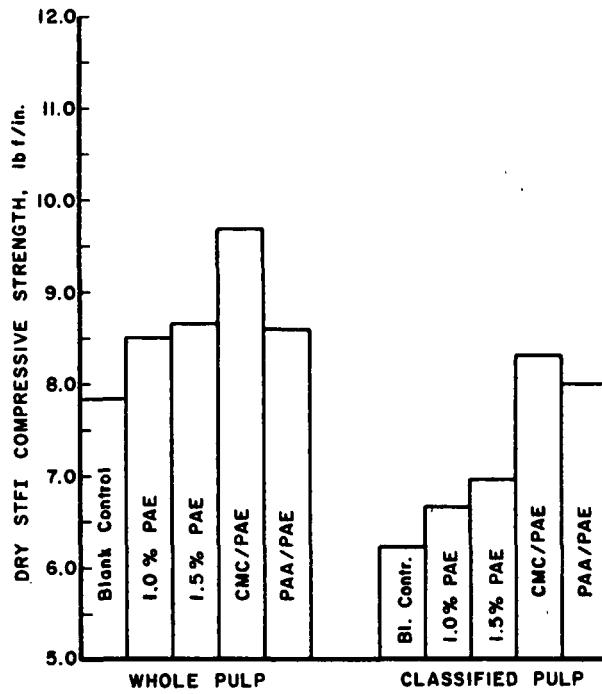


Figure 46. Dry STFI compressive strength - softwood bleached kraft.

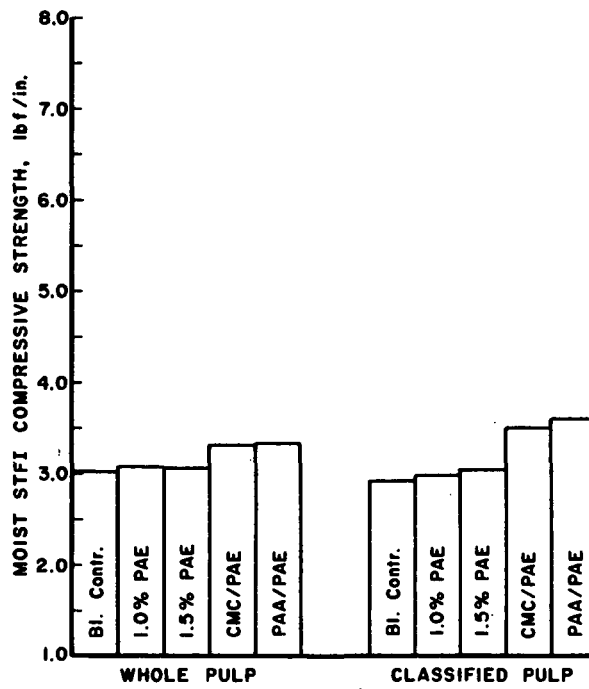


Figure 47. Moist STFI compressive strength - softwood bleached kraft.

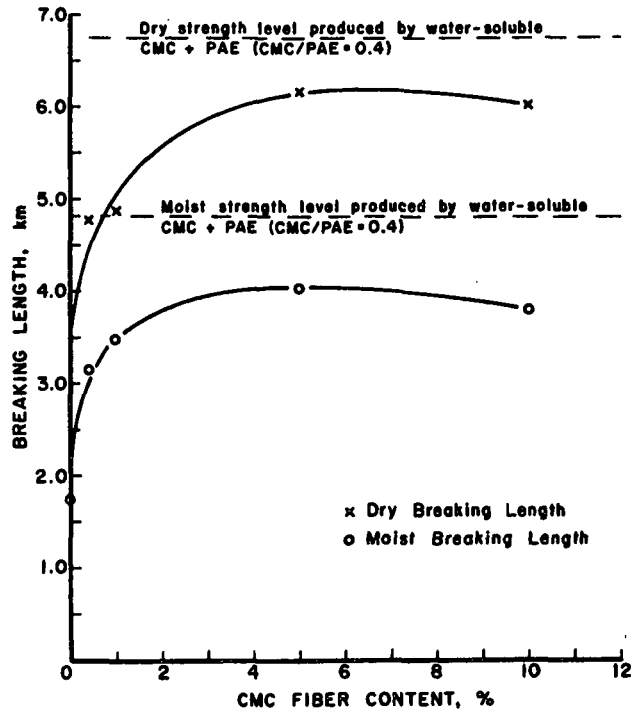


Figure 48. The effect of CMC fiber content on breaking length - bl. softwood kraft with 1% PAE added.

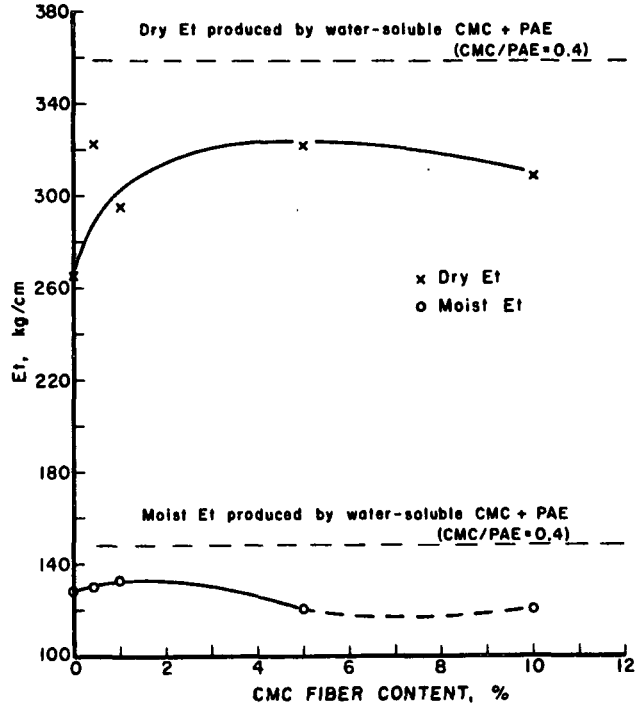


Figure 49. The effect of CMC fiber content on Et - Bl. softwood kraft with 1% PAE added.

For purposes of reference, handsheets were also formed from the whole pulp with addition of PAE, CMC/PAE, and PAA/PAE. Results for this series are presented in Table 12. Breaking length and Et as a function of untreated fines addition are shown in Fig. 50 and 51. Note that moist strength properties in Table 12 were determined at two relative humidity conditions, 91-93 and 88-89%. The lower humidity resulted in sheet moisture contents which were closer to those encountered with the kraft pulps.

A similar fines-additive study was conducted with the once-dried average yield unbleached softwood kraft pulp (Pulp No. 4). In this case the whole pulp contained 12% of fines and the readdition steps were 4, 8, 12, and 24%. Also, in the bonding agent part of the study, the addition of treated or untreated fines was 12%. Results for this series are presented in Table 13, and the effect of treated fines addition on strength properties is shown in Fig. 52 and 53.

#### ANALYSIS OF POLYMER-FIBER BONDING MECHANISMS

The use of diffuse reflectance FTIR analysis of polymer treated papers was continued using handsheets from pulps differing in yield and wood source. In the initial series the additives were applied by immersing in aqueous solutions of the additives under controlled conditions followed by drying 10 minutes at 105°C. The ratio of the 1740 ester band/1650 amide band was measured, and the results are recorded in Table 14.

In pursuing the analysis of bonded papers, further efforts were made to determine if a satisfactory definition of bonding mechanisms could be achieved through diffuse reflectance FTIR when the bonding agents were added to the fiber before sheet formation. In this direction, handsheets were prepared from two average-yield classified unbleached kraft pulps (No. 2 and 4) under conditions where covalent bonding could or could not occur.

Table 12. The effect of fines and bonding agents on strength properties - softwood TMP. a

Set No.	Description-Additives, % based on Fiber or Fines	Basis Wt. %	Thickness, $\mu\text{m}$	Apparent Density, g/cc	Breaking Length, km		TEA, $\text{kgm/m}^2$		Et, kg/cm		Stretch, %	
					Av.	SD	Av.	SD	Av.	SD	Av.	SD
61	Blank control - whole pulp	63.7	184	0.346	3.24	0.106	2.43	0.301	222	22.5	1.85	0.142
66	Blank control - classified pulp	62.5	264	0.236	1.28	0.062	0.697	0.101	97.7	4.9	1.38	0.105
109	Classified pulp + 5% of untreated fines	62.4	247	0.252	1.65	0.085	0.885	0.129	122	6.2	1.40	0.129
110	Classified pulp +10% of untreated fines	63.0	237	0.266	2.03	0.048	1.27	0.089	144	4.3	1.59	0.058
111	Classified pulp +20% of untreated fines	63.2	215	0.294	2.56	0.048	1.53	0.070	190	7.6	1.44	0.096
112	Classified pulp +30% of untreated fines	62.8	195	0.322	3.13	0.097	1.93	0.268	226	15.5	1.52	0.160
113	Classified pulp +60% of untreated fines	63.8	166	0.385	3.86	0.125	2.57	0.421	284	19.5	1.61	0.187
Classified Pulp + 30% of Treated Fines												
----- Treatments -----												
114	PAE, 1.5	62.5	198	0.316	3.28	0.074	2.42	0.252	222	10.9	1.81	0.131
115	PAE, 1.0; CMC, 0.4	63.6	199	0.319	3.31	0.096	2.61	0.174	216	19.4	1.88	0.078
116	PAE, 1.0; PAA, 0.2	63.4	196	0.324	2.98	0.146	2.17	0.377	211	14.8	1.74	0.175
117	PAE, 1.0; CMC, 0.4b	63.6	192	0.331	3.90	0.177	2.99	0.431	250	4.3	1.89	0.172
Treated Classified Pulp + 30% of Untreated Fines												
----- Treatments -----												
118	PAE, 1.5	62.7	192	0.326	3.96	0.216	3.32	0.226	234	16.0	2.06	0.101
119	PAE, 1.0; CMC, 0.4	64.2	198	0.324	4.09	0.237	3.45	0.526	265	15.6	2.02	0.191
120	PAE, 1.0; PAA, 0.2	63.7	196	0.324	3.53	0.179	2.86	0.445	238	14.7	1.92	0.171
121	PAE, 1.0; CMC, 0.4c	63.6	186	0.341	4.44	0.154	3.85	0.526	268	9.2	2.10	0.203
Treated Classified Pulp + 30% of Treated Fines												
----- Treatments -----												
122	PAE, 1.5	63.2	199	0.318	3.92	0.147	3.57	0.442	235	20.4	2.18	0.197
123	PAE, 1.0; CMC, 0.4	63.9	198	0.323	4.41	0.154	4.18	0.275	238	12.7	2.28	0.104
124	PAE, 1.0; PAA, 0.2	63.7	192	0.331	3.89	0.207	3.32	0.572	242	19.6	2.02	0.220
63	Whole pulp, PAE, 1.5	65.5	202	0.324	3.22	0.106	2.80	0.199	202	7.9	2.07	0.095
64	Whole pulp, PAE, 1.0; CMC, 0.4	63.4	184	0.344	3.88	0.070	3.12	0.350	218	13.6	2.06	0.146
65	Whole pulp, PAE, 1.0; PAA, 0.2	62.8	188	0.334	3.41	0.136	2.55	0.347	194	15.2	2.01	0.200

Table 12 (Continued). The effect of fines and bonding agents on strength properties - softwood TMP.<sup>a</sup>

Set No.	Description-Additives, % Based on Fiber or Fines	Moisture Content, %	Moist Strength Properties				Moist Tensile Factor				
			Breaking Length, km	TEA, kgm/m <sup>2</sup>	Et, kg/cm	Stretch, %					
			AV.	SD	AV.	SD	AV.	SD			
61	Blank control - whole Pulp	17.3	1.70	0.182	2.36	0.248	111.0	5.98	3.10	0.200	1.00
66	Blank control - classified pulp	17.6	0.648	0.057	0.519	0.039	45.0	2.17	2.11	0.214	0.38
109	Classified pulp + 5% of untreated fines	17.3	0.803	0.051	0.763	0.082	52.8	3.10	2.25	0.138	0.47
110	Classified pulp +10% of untreated fines	18.1	0.889	0.062	0.879	0.101	53.8	1.57	2.37	0.140	0.52
111	Classified pulp +20% of untreated fines	18.3	1.15	0.101	1.38	0.180	69.9	4.88	2.74	0.177	0.68
112	Classified pulp +30% of untreated fines	18.5	1.44	0.108	1.84	0.336	83.0	4.75	2.98	0.312	0.85
113	Classified pulp +60% of untreated fines	18.9	1.74	0.047	2.95	0.339	92.5	5.68	3.86	0.429	1.02
Classified Pulp + 30% of Treated Fines											
----- Treatments -----											
114	PAE, 1.5	18.2	2.02	0.158	3.06	0.383	73.2	2.28	3.97	0.213	1.20
115	PAE, 1.0; CMC, 0.4	18.4	1.90	0.056	2.85	0.108	75.8	2.97	3.82	0.197	1.11
116	PAE, 1.0; PAA, 0.2	18.2	1.81	0.110	2.80	0.272	75.2	2.96	3.83	0.177	1.06
117	PAE, 1.0; CMC, 0.4 <sup>b</sup>	17.6	2.56	0.118	4.22	0.425	87.1	4.27	4.28	0.306	1.27
Treated Classified Pulp + 30% of Untreated Fines											
----- Treatments -----											
118	PAE, 1.5	18.3	2.55	0.202	3.88	0.404	75.3	7.73	4.23	0.081	1.50
119	PAE, 1.0; CMC, 0.4	18.3	2.61	0.108	4.17	0.374	79.1	3.84	4.42	0.240	1.53
120	PAE, 1.0; PAA, 0.2	18.4	2.02	0.202	2.88	0.446	82.4	8.62	3.63	0.150	1.20
121	PAE, 1.0; CMC, 0.4 <sup>c</sup>	17.2	2.88	0.122	4.79	0.474	94.0	4.08	4.37	0.274	1.69
Treated Classified Pulp + 30% of Treated Fines											
----- Treatments -----											
122	PAE, 1.5	17.9	2.44	0.063	3.94	0.365	71.3	2.60	4.37	0.335	1.43
123	PAE, 1.0; CMC, 0.4	17.8	2.90	0.161	5.08	0.296	71.2	4.16	4.87	0.156	1.70
124	PAE, 1.0; PAA, 0.2	18.0	2.36	0.053	3.85	0.281	77.1	3.89	4.19	0.165	1.39
63	Whole pulp, PAE, 1.5	17.3	1.85	0.284	2.96	0.863	80.7	4.76	4.00	0.737	1.09
64	Whole pulp, PAE, 1.0; CMC, 0.4	17.0	2.79	0.116	4.44	0.328	124	4.82	4.08	0.144	1.64
65	Whole pulp, PAE, 1.0; PAA, 0.2	16.9	2.54	0.288	3.22	0.381	97	11.2	3.60	0.200	1.49

Table 12 (Continued). The effect of fines and bonding agents on strength properties - softwood TMP. a

Set No.	Description-Additives, % based on Fiber or Fines	Moisture Content, %	Moist Strength Properties						Moist Tensile Factor		
			Breaking Length, km		TEA, kgm/m <sup>2</sup>		Et, kg/cm			Stretch, %	
			Av.	SD	Av.	SD	Av.	SD	Av.	SD	
61	Blank control - whole pulp	15.8	2.06	0.088	2.68	0.284	120	7.6	2.99	0.180	1.00
66	Blank control - classified pulp	15.3	0.79	0.063	0.578	0.099	67.3	2.8	1.55	0.672	1.39
109	Classified pulp + 5% of untreated fines	15.5	1.00	0.065	0.763	0.171	68.8	3.0	1.79	0.272	1.49
110	Classified pulp +10% of untreated fines	15.4	1.35	0.079	1.53	0.150	129	9.7	2.60	0.157	1.66
111	Classified pulp +20% of untreated fines	15.4	2.25	0.507	3.08	1.110	118	6.6	3.11	0.603	1.09
112	Classified pulp +30% of untreated fines	15.7	2.22	0.113	2.76	0.334	133	9.4	2.88	0.274	1.08
113	Classified pulp +60% of untreated fines	15.9	2.62	0.057	4.07	0.129	145	2.8	3.57	0.083	1.27
Classified Pulp + 30% of Treated Fines											
----- Treatments -----											
114	PAE, 1.5	15.8	2.60	0.083	3.73	0.389	112	4.7	3.59	0.238	1.26
115	PAE, 1.0; CMC, 0.4	15.5	2.54	0.042	3.65	0.228	117	2.8	3.48	0.145	1.23
116	PAE, 1.0; PAA, 0.2	15.4	2.49	0.121	3.34	0.319	123	3.7	3.27	0.187	1.21
117	PAE, 1.0; CMC, 0.4 <sup>b</sup>	15.4	3.02	0.040	4.58	0.144	125	2.4	3.83	0.083	1.47
Treated Classified Pulp + 30% of Untreated Fines											
----- Treatments -----											
118	PAE, 1.5	15.2	3.14	0.195	4.51	0.434	119	9.9	3.73	0.237	1.52
119	PAE, 1.0; CMC, 0.4	16.0	3.20	0.087	5.13	0.361	122	6.9	4.13	0.192	1.55
120	PAE, 1.0; PAA, 0.2	16.0	2.60	0.124	3.71	0.370	117	7.4	3.55	0.220	1.26
121	PAE, 1.0; CMC, 0.4 <sup>c</sup>	15.4	3.40	0.145	4.92	0.458	137	4.7	3.73	0.189	1.65
Treated Classified Pulp + 30% of Treated Fines											
----- Treatments -----											
122	PAE, 1.5	15.7	3.20	0.113	4.77	0.438	119	9.6	3.90	0.233	1.55
123	PAE, 1.0; CMC, 0.4	15.5	3.66	0.140	5.80	0.552	126	4.1	4.15	0.295	1.78
124	PAE, 1.0; PAA, 0.2	16.0	3.01	0.108	4.32	0.313	126	6.1	3.63	0.138	1.46
63	Whole pulp, PAE, 1.5	15.4	2.76	0.064	4.17	0.442	112	6.1	3.70	0.377	1.34
64	Whole pulp, PAE, 1.0; CMC, 0.4	15.4	3.26	0.140	4.87	0.339	123	5.6	3.84	0.120	1.58
65	Whole pulp, PAE, 1.0; PAA, 0.2	15.5	2.73	0.089	4.17	0.181	106	11.3	3.84	0.120	1.33

Table 12 (Continued). The effect of fines and bonding agents on strength properties - softwood TMP.<sup>a</sup>

Set No.	Description-Additives, % Based on Fiber or Fines	Wet Breaking Length, km		Wet Tensile Factor
		Av.	SD	
61	Blank controls - whole pulp	0.148	0.020	1.00
66	Blank controls - classified pulp	0.048	0.006	0.32
109	Classified pulp + 5% of untreated fines	0.071	0.003	0.48
110	Classified pulp +10% of untreated fines	0.072	0.007	0.49
111	Classified pulp +20% of untreated fines	0.109	0.006	0.74
112	Classified pulp +30% of untreated fines	0.141	0.008	0.95
113	Classified pulp +60% of untreated fines	0.150	0.012	1.01
Classified Pulp + 30% of Treated Fines				
----- Treatments -----				
114	PAE, 1.5	0.962	0.007	6.5
115	PAE, 1.0; CMC, 0.4	0.826	0.026	5.6
116	PAE, 1.0; PAA, 0.2	0.650	0.020	4.4
117	PAE, 1.0; CMC, 0.4 <sup>b</sup>	1.460	0.065	9.9
Treated Classified Pulp + 30% of Untreated Fines				
----- Treatments -----				
118	PAE, 1.5	1.570	0.105	10.6
119	PAE, 1.0; CMC, 0.4	1.340	0.088	9.0
120	PAE, 1.0; PAA, 0.2	0.746	0.035	5.0
121	PAE, 1.0; CMC, 0.4 <sup>c</sup>	1.630	0.054	11.0
Treated Classified Pulp + 30% of Treated Fines				
----- Treatments -----				
122	PAE, 1.5	1.60	0.056	10.8
123	PAE, 1.0; CMC, 0.4	1.99	0.075	13.4
124	PAE, 1.0; PAA, 0.2	1.32	0.042	8.9
63	Whole pulp, PAE, 1.5	1.33	0.068	9.0
64	Whole pulp, PAE, 1.0; CMC, 0.4	1.57	0.103	10.6
65	Whole pulp, PAE, 1.0; PAA, 0.2	1.25	0.047	8.4

<sup>a</sup>Hemlock; 30% of fines in whole pulp.

<sup>b</sup>Fines treated with CMC/PAE in an amount equiv. to that added to whole pulp.

<sup>c</sup>Class fiber treated with CMC/PAE in an amount equiv. to that added to whole pulp.

<sup>d</sup>Moisture content at 91-93% RH.

<sup>e</sup>Moisture content at 88-89% RH.

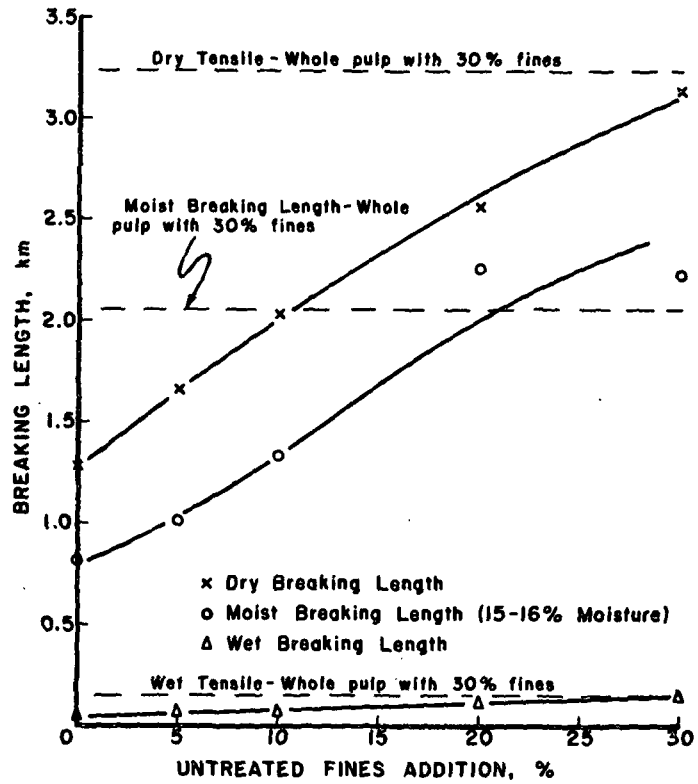


Figure 50. The effect of fines on tensile strength (hemlock TMP).

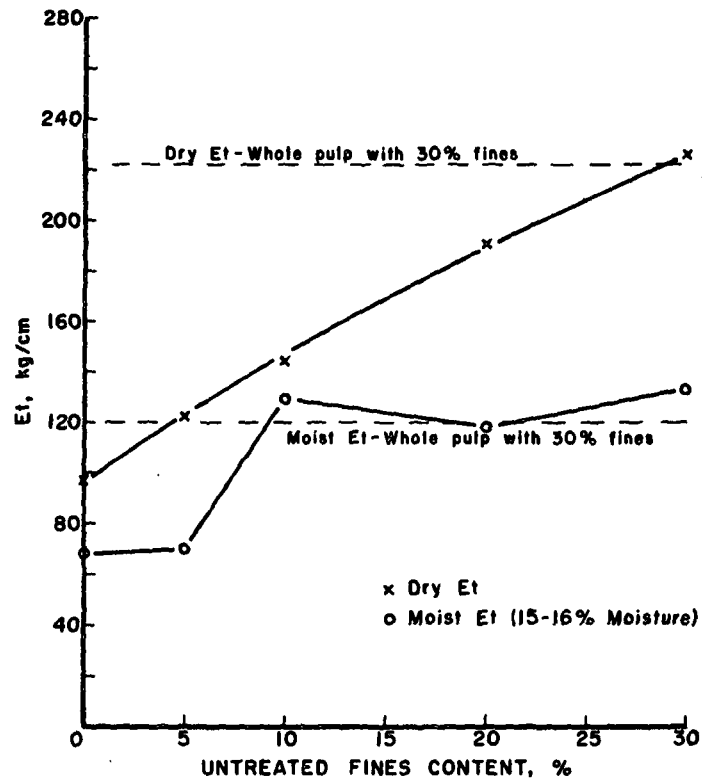


Figure 51. The effect of fines on Et (hemlock TMP).

Table 13. The effect of fines and bonding agents on strength properties - av. yield softwood unbleached kraft.

Set No.	Basis, Wt. g/m <sup>2</sup>	Apparent Density, g/cc	Dry Strength Properties								
			Breaking Length, km		TEA, kgm/m <sup>2</sup>		Et, kg/cm		Stretch, %		
			Av.	SD	Av.	SD	Av.	SD	Av.	SD	
80	Blank controls - whole pulp	63.9	0.484	5.20	0.196	7.93	0.939	385	6.4	3.3	0.25
47	Blank controls - classified pulp	62.9	0.447	3.83	0.284	4.51	0.563	316	33.5	2.6	0.26
125	Classified pulp + 4% of untreated fines	64.9	0.455	4.01	0.217	5.09	0.742	330	15.3	2.7	0.23
126	Classified pulp + 8% of untreated fines	62.7	0.452	4.54	0.226	5.49	0.737	349	14.8	2.7	0.23
127	Classified pulp + 12% of untreated fines	62.4	0.464	4.91	0.148	6.17	0.929	364	14.6	2.8	0.34
128	Classified pulp + 24% of untreated fines	62.8	0.497	5.39	0.188	7.97	0.379	380	20.3	3.3	0.23
Classified Pulp + 12% of Treated Fines											
----- Treatments -----											
129	PAE, 1.5	62.6	0.480	5.35	0.356	7.57	1.61	370	15.1	3.2	0.49
130	PAE, 1.0; CMC, 0.4	61.6	0.481	5.28	0.218	7.22	1.015	361	8.5	3.1	0.31
131	PAE, 1.0; PAA, 0.2	61.1	0.477	5.46	0.195	8.00	0.422	358	15.3	3.4	0.12
132	PAE, 1.0; CMC, 0.4 <sup>a</sup>	63.8	0.493	6.92	0.664	11.03	2.366	415	22.4	3.7	0.49
Treated Classified Pulp + 12% of Untreated Fines											
----- Treatments -----											
133	PAE, 1.5	62.7	0.502	7.09	0.263	10.57	0.448	421	9.7	3.5	0.12
134	PAE, 1.0; CMC, 0.4	64.4	0.520	7.68	0.326	14.03	0.983	426	23.0	4.2	0.20
135	PAE, 1.0; PAA, 0.2	64.1	0.503	7.42	0.326	12.61	0.682	442	26.5	3.9	0.14
136	PAE, 1.0; CMC, 0.4 <sup>b</sup>	61.1	0.505	7.92	0.593	12.88	1.461	429	29.9	4.0	0.22
Treated Classified Pulp + 12% of Treated Fines											
----- Treatments -----											
137	PAE, 1.5	61.7	0.494	6.75	0.293	9.25	0.674	414	25.9	3.3	0.19
138	PAE, 1.0; CMC, 0.4	61.6	0.514	7.47	0.107	12.30	0.580	402	8.1	4.0	0.19
139	PAE, 1.0; PAA, 0.2	63.3	0.517	6.79	0.300	10.64	1.410	412	15.3	3.6	0.35
82	Whole pulp; PAE, 1.5	62.8	0.485	6.31	0.268	9.47	0.757	395	18.0	3.5	0.22
83	Whole pulp; PAE, 1.0; CMC, 0.4	61.8	0.501	7.35	0.085	13.05	0.747	397	15.3	4.3	0.24
84	Whole pulp; PAE, 1.0; PAA, 0.2	61.2	0.506	6.97	0.284	11.0	1.09	410	6.7	3.8	0.24

Table 13 (Continued). The effect of fines and bonding agents on strength properties - av. yield softwood unbleached kraft.

Set No.	Description of Additives or Fines, % based on fiber	Moisture Content, % (91-93% RH)	Moist Strength Properties						Moist Tensile Factor	Wet Breaking Length, km	Wet Tensile Factor			
			Breaking Length, km	TEA, kg/m <sup>2</sup>	Et, kg/cm	Stretch, %	Av.	SD						
80	Blank control - whole pulp	15.3	2.84	0.224	5.52	0.708	141	4.7	4.7	0.37	--	0.191	0.010	1.00
47	Blank control - classified pulp	15.9	1.88	0.082	3.09	0.354	111	9.3	3.9	0.40	0.66	0.129	0.008	0.68
125	Classified pulp + 4% of untreated fines	16.4	2.00	0.060	3.43	0.179	123	3.5	3.8	0.22	0.70	0.161	0.008	0.84
126	Classified pulp + 8% of untreated fines	15.9	2.37	0.172	4.47	0.270	125	10.9	4.3	0.15	0.83	0.172	0.011	0.90
127	Classified pulp + 12% of untreated fines	15.5	2.49	0.182	5.04	0.663	124	10.2	4.6	0.51	0.88	0.207	0.012	1.08
128	Classified pulp + 24% of untreated fines	16.1	3.26	0.247	6.96	0.845	147	6.3	5.0	0.19	1.15	0.244	0.012	1.28
Classified Pulp + 12% of Treated Fines														
----- Treatments -----														
129	PAE, 1.5	15.7	3.32	0.191	7.36	1.015	133	10.5	5.4	0.39	1.17	0.690	0.040	3.61
130	PAE, 1.0; CMC, 0.4	15.9	3.25	0.178	6.40	0.399	135	5.9	4.9	0.23	1.14	0.573	0.013	3.00
131	PAE, 1.0; PAA, 0.2	15.7	3.37	0.146	6.74	0.224	136	10.5	5.0	0.22	1.19	0.615	0.024	3.22
132	PAE, 1.0; CMC, 0.4 <sup>a</sup>	15.1	4.82	0.166	10.44	0.548	160	11.9	5.8	0.17	1.70	1.92	0.126	10.0
Treated Classified Pulp + 12% of Untreated Fines														
----- Treatments -----														
133	PAE, 1.5	16.8	4.87	0.291	10.84	1.025	141	12.6	6.3	0.24	1.17	2.44	0.132	12.8
134	PAE, 1.0; CMC, 0.4	16.8	5.24	0.205	11.74	0.151	142	12.8	6.3	0.13	1.85	2.33	0.147	12.2
135	PAE, 1.0; PAA, 0.2	16.0	4.86	0.122	10.84	0.711	163	3.0	5.8	0.25	1.71	1.70	0.146	8.9
136	PAE, 1.0; CMC, 0.4 <sup>b</sup>	16.3	5.28	0.302	10.85	1.204	154	9.6	5.9	0.24	1.86	2.28	0.028	11.9
Treated Classified Pulp + 12% of Treated Fines														
----- Treatments -----														
137	PAE, 1.5	16.4	4.81	0.260	9.96	1.050	145	13.1	5.8	0.29	1.69	2.32	0.188	12.1
138	PAE, 1.0; CMC, 0.4	16.6	5.31	0.266	10.91	1.190	147	9.2	6.0	0.43	1.87	2.36	0.092	12.3
139	PAE, 1.0; PAA, 0.2	16.7	4.96	0.158	10.14	0.766	162	4.0	5.7	0.22	1.75	2.08	0.095	10.9
82	Whole pulp; PAE, 1.5	15.4	4.48	0.188	8.95	0.429	132	8.6	5.8	0.20	1.58	2.13	0.197	11.2
83	Whole pulp; PAE, 1.0; CMC, 0.4	15.3	5.17	0.244	11.39	0.856	140	3.3	6.4	0.20	1.82	2.19	0.090	11.5
84	Whole pulp; PAE, 1.0; PAA, 0.2	15.8	4.60	0.152	9.77	0.763	135	11.0	6.2	0.28	1.62	1.91	0.070	10.0

<sup>a</sup>Fines treated with CMC/PAE in an amount equivalent to that added to whole pulp.

<sup>b</sup>Classified fiber treated with CMC/PAE in an amount equivalent to that added to whole pulp.

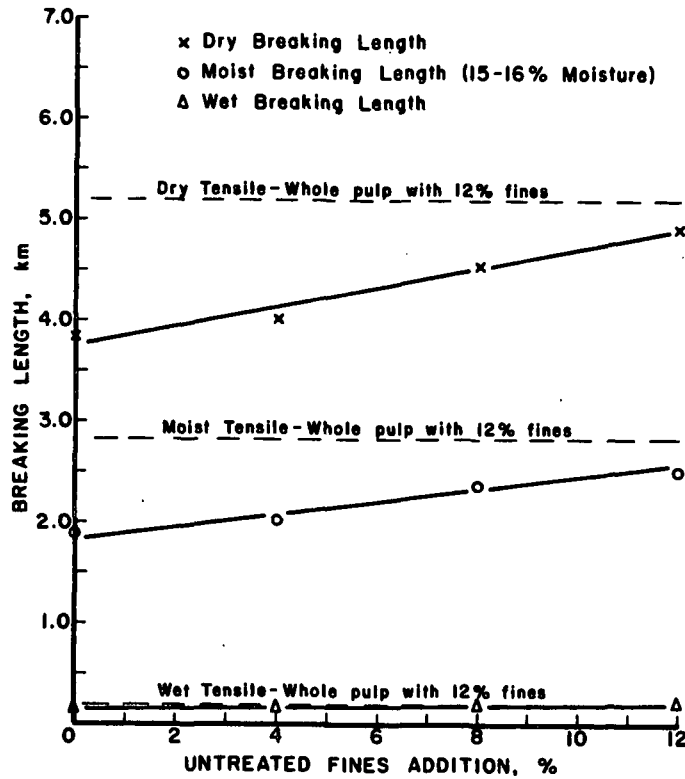


Figure 52. The effect of fines on tensile strength (southern pine unbl. kraft).

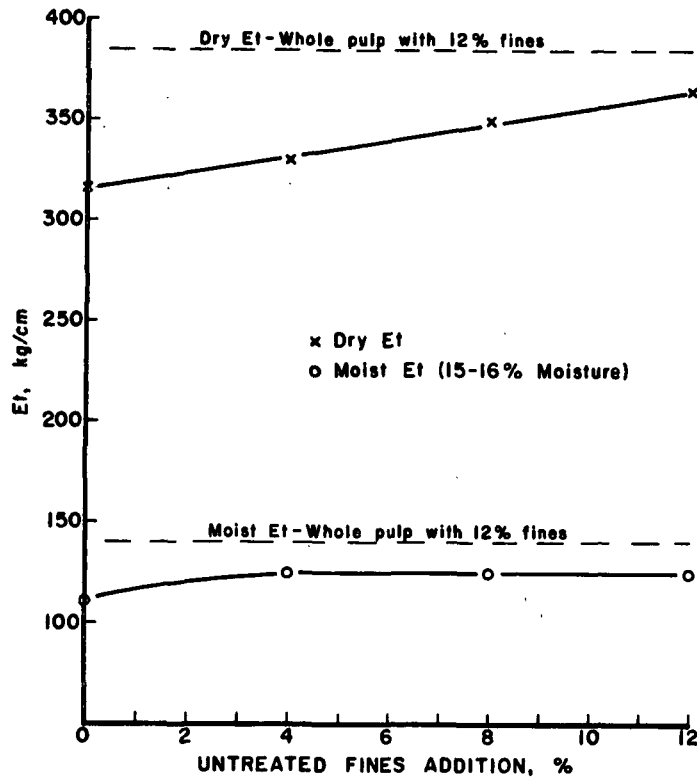


Figure 53. The effect of fines on Et (southern pine unbl. kraft).

Table 14. FTIR analysis of handsheets treated by immersion with polymer combinations.

Test No.	Pulp Used in Hand-sheet Preparations	Additives, % solids	FTIR analysis; A1740(Ester)/A1650(Amide)
	47-48% Yield softwood unbl. kr., beaten and classified		
1		PAE,1.0	0.275
2		PAE,1.0;CMC, 0.4	0.436
3		PAE,1.0;PAA, 0.2	0.668
4		1:1 Starch:PAE,1.0;PAA,0.1	0.722
	49% Yield softwood unbl. kr., beaten and classified		
5		PAE,1.0	0.268
6		PAE,1.0;CMC,0.4	0.610
7		PAE,1.0;PAA,0.2	0.416
8		1:1 Starch:PAE,1.0;PAA,0.1	0.417
	57% Yield softwood unbl. kr., beaten and classified		
9		PAE,1.0	0.267
10		PAE,1.0;CMC,0.4	0.395
11		PAE,1.0;PAA,0.2	0.589
12		1:1 Starch:PAE,1.0;PAA,0.1	0.398
	88% Yield softwood TMP <sup>a</sup> beaten 10 min, classified		
13		PAE,1.0	0.102
14		PAE,1.0;CMC,0.4	0.213
15		PAE,1.0;PAA,0.2	0.239
16		1:1 Starch:PAE,1.0;PAA,0.1	0.158
	88% Yield softwood TMP <sup>a</sup> beaten 10 min, whole pulp		
17		PAE,1.0	0.173
18		PAE,1.0;CMC,0.4	0.316
19		PAE,1.0;PAA,0.2	0.329
20		1:1 Starch:PAE,1.0;PAA,0.1	0.342
	45-46% Yield softwood unbl. kr., beaten, whole pulp		
21		PAE,1.0	0.192
22		PAE,1.0;CMC,0.4	0.329
23		PAE,1.0;PAA,0.2	0.329

<sup>a</sup>Ester band evident in blank controls; this may cause some interference in the FTIR analysis.

A brief series of tests was carried out using softwood unbleached kraft (Pulp No. 2). These tests involved the addition of polyethyleneimine (PEI) alone and in combination with PSFA or PAA. In theory, covalent bonding could not occur with PEI or PEI/PSFA. However, covalent bonding could conceivably occur in the presence of PAA/PEI through ester formation with cellulose hydroxyls. The strength and analytical results for this brief series are presented in Table 15.

A more extensive examination of polymer combinations, their effects on strength properties, and possible bonding mechanisms are presented in Table 16. This series involved the use of PEI and PDDAC (polydiallyl dimethyl ammonium chloride) in classified Pulp No. 4. The latter was used alone and in combination with PAA at pH 4 and with PSFA and PAA at pH 7-9. The formation of ester bonds and, hence, covalent bonding had been established previously for the CMC/PAE and PAA/PAE combinations, and hence these tests were not repeated in this series.

#### EXTERNAL TREATMENTS WITH POLYSTYRENE

Blank handsheets prepared from the (whole) once-dried softwood unbleached kraft (Pulp No. 4) were immersed in 10 and 20% polystyrene solutions in toluene. After 10 seconds immersion, the sheets were allowed to drain and excess solution was removed by light blotting. The treated papers were drum dried in the usual manner and then submitted for the full range of physical tests. Results are recorded in Table 17.

Table 15. Strength properties and bonding mechanisms (47.2% yield softwood unbleached kraft - classified).

Set No.	Additives, % based on fiber	pH in Sheetmold	Basis Wt., g/m <sup>2</sup>	Apparent Density, g/cc	Dry Strength Properties									
					Breaking Length, km		TEA, kgm/m <sup>2</sup>		Et, kg/cm		Stretch, %			
					Av.	SD	Av.	SD	Av.	SD	Av.	SD		
140	Blank controls	7-9	61.7	0.370	2.63	0.091	1.88	0.377	248	23.6	1.7	0.29		
141	PAE, 1.0	7-9	62.7	0.386	4.50	0.389	4.91	0.389	273	12.3	2.6	0.24		
142	PAE, 1.0; CMC, 0.4	7-9	63.9	0.406	6.63	0.471	8.72	0.810	344	20.7	3.4	0.16		
143	PEI, 1.0	7-9	66.8	0.416	3.49	0.181	3.24	0.465	342	10.5	2.0	0.14		
144	PEI, 1.0; PSFA, 0.2	7-9	64.8	0.414	3.93	0.442	4.36	1.15	334	18.9	2.5	0.40		
145	PEI, 1.0; PAA, 0.2	7-9	69.0	0.419	4.44	0.629	5.13	1.402	388	25.8	2.4	0.36		

Set No.	Additives % based on fiber	Moisture Content, % at (91-93% RH)	Moist strength properties								Moist Tensile Factor	Dry STFI Compressive Strength, lb f/inch				
			Breaking Length, km		TEA, kgm/m <sup>2</sup>		Et, kg/cm		Stretch, %			Wet Breaking Length, km	Wet Tensile Factor	Strength, lb f/inch		
			Av.	SD	Av.	SD	Av.	SD	Av.	SD				Av.	SD	
140	Blank control	17.3	1.14	0.110	1.33	0.175	96.8	10.47	2.6	0.21	1.00	0.083	0.010	1.00	5.30	0.309
141	PAE, 1.0	16-17	2.52	0.187	4.84	0.371	124	4.95	3.4	0.15	2.21	0.92	0.057	11.08	--	--
142	PAE, 1.0; CMC, 0.4	16-17	3.44	0.133	7.52	0.452	124	16.4	4.8	0.09	2.57	0.24	0.049	14.94	--	--
143	PEI, 1.0	17.5	1.86	0.042	2.94	0.166	119	10.8	3.5	0.21	1.63	0.491	0.043	5.91	7.89	0.738
144	PEI, 1.0; PSFA, 0.4	16.9	2.25	0.222	3.71	0.488	115	12.7	3.9	0.19	1.97	0.607	0.075	7.31	8.19	0.623
145	PEI, 1.0; PAA, 0.2	17.5	2.34	0.164	4.35	0.251	131	9.3	4.1	0.34	2.05	0.567	0.035	6.83	9.25	1.010

Set No.	Additives, % based on fiber	Moist STFI Compressive Strength, lb f/inch		Moist Compressive Strength, factor	Diffuse Reflectance FTIR Analysis, Absorbance Peaks Occuring at Amine 1650 cm <sup>-1</sup> , Av. area under curve	Comments
		Av.	SD			
140	Blank controls	2.92	0.286	1.00	--	--
141	PAE, 1.0	--	--	--	--	--
142	PAE, 1.0; CMC, 0.4	--	--	--	--	--
143	PEI, 1.0	3.43	0.393	1.17	2.33	No evidence of ester formation
144	PEI, 1.0; PSFA, 0.2	3.34	0.236	1.14	3.04	No evidence of ester formation; broad band at 1700-1600 cm <sup>-1</sup>
145	PEI, 1.0; PAA, 0.2	3.88	0.353	1.33	3.04	No evidence of ester formation; broad band at 1700-1600 cm <sup>-1</sup>

Table 16. Strength properties and bonding mechanisms. (Once-dried and classified softwood unbleached kraft.)

Set No.	Additives, % based on fiber	pH in Sheetmold	Basis Wt., g/m <sup>2</sup>	Apparent Density, g/cc	Breaking Length, km	Dry Strength Properties						
						Av.	SD	TGA, kg/m <sup>2</sup>	Et, kg/cm	Stretch, %		
47	Blank controls	7-9	62.9	0.447	3.83	0.284	4.51	0.563	316	33.5	2.6	0.26
48	PAE, 1.0	7-9	65.8	0.442	5.27	0.361	7.46	0.954	357	26.6	3.2	0.21
49	PAE, 1.5	7-9	61.4	0.447	5.38	0.368	7.64	1.236	313	5.7	3.5	0.36
50	PAE, 1.0; CMC, 0.4	7-9	64.9	0.484	7.27	0.531	12.2	1.41	409	22.2	4.0	0.22
51	PAE, 1.0; PAA, 0.2	7-9	64.7	0.466	6.14	0.38	10.4	1.01	368	24.9	3.9	0.27
146	PEI, 1.0	7-9	70.4	0.478	5.00	0.295	7.09	1.014	400	19.4	2.9	0.27
147	PEI, 1.0; PAA, 0.2	7-9	79.6	0.490	5.86	0.252	10.9	1.07	480	9.6	3.4	0.21
148	PDDAC, 0.5	7-9	67.4	0.461	3.89	0.142	5.22	0.372	308	11.8	2.8	0.12
149	PDDAC, 1.0	7-9	64.8	0.460	3.81	0.204	5.06	0.564	284	19.1	2.9	0.17
150	PDDAC, 0.5; PSFA, 0.2	7-9	67.8	0.454	4.06	0.212	5.16	0.709	325	17.0	2.6	0.25
151	PDDAC, 0.5; PSFA, 0.5	7-9	69.9	0.444	5.12	0.315	8.17	0.484	363	25.9	3.3	0.06
152	PDDAC, 1.0; PSFA, 0.2	7-9	69.3	0.455	3.85	0.197	5.80	0.754	312	17.0	3.0	0.24
153	PDDAC, 1.0; PSFA, 0.5	7-9	68.3	0.450	4.15	0.229	5.47	0.733	329	17.3	2.7	0.21
154	PDDAC, 0.5; PAA, 0.2	7-9	71.2	0.455	4.92	0.388	8.98	0.826	338	34.7	3.7	0.23
155	PDDAC, 0.5; PAA, 0.5	7-9	67.4	0.464	5.06	0.226	8.56	1.150	334	15.4	3.6	0.35
156	PEI, 1.0; PAA, 0.2	4.0	70.3	0.451	5.48	0.648	9.37	1.183	381	41.9	3.6	0.11
157	PDDAC, 0.2; PAA, 0.2	4.1	63.7	0.438	4.75	0.299	6.44	0.595	331	22.7	3.1	0.13
158	PDDAC, 0.5; PAA, 0.2	4.1	63.4	0.441	4.53	0.208	5.94	0.744	320	11.4	3.0	0.27
159	PDDAC, 0.5; PAA 0.5	4.1	68.7	0.443	5.23	0.111	8.32	0.355	370	8.0	3.3	0.12

Table 16 (Continued). Strength properties and bonding mechanisms. (Once-dried and classified softwood unbleached kraft.)

Set No.	Additives, % based on fiber	Moisture Content, %	Moist Strength Properties						Wet Breaking		Wet Tensile Factor	Dry STFI Compressive				
			Breaking Length, km	TEA, kgm/m <sup>2</sup>	Et, kg/cm	Stretch, %	Moist Tensile Factor	Length, km	Factor	Strength, lb f/inch		SD				
			Av.	SD	Av.	SD	Av.	SD	Av.	SD		Av.	SD			
47	Blank controls	15.9	1.08	0.082	3.09	0.354	111	9.3	3.9	0.40	1.00	0.129	0.008	1.0	7.13	0.777
48	PAB, 1.0	15.2	3.64	0.326	7.74	1.030	129	5.1	5.1	0.35	1.94	1.27	0.152	9.8	8.79	0.872
49	PAB, 1.5	14.8	3.73	0.199	7.54	0.557	120	7.6	5.3	0.28	1.98	1.66	0.095	12.9	8.36	0.777
50	PAB, 1.0; CMC, 0.4	15.5	4.78	0.458	11.92	1.050	142	5.5	6.2	0.28	2.54	2.30	0.138	17.8	10.12	0.813
51	PAB, 1.0; PAA, 0.2	15.5	4.17	0.264	9.21	0.718	125	11.9	5.8	0.30	2.22	1.73	0.112	13.4	8.97	0.641
146	PEI, 1.0	14.8	3.36	0.200	6.92	0.473	168	12.4	4.8	0.15	1.79	0.862	0.061	6.7	9.11	0.548
147	PEI, 1.0; PAA, 0.2	15.1	3.62	0.099	9.18	0.531	185	7.5	5.3	0.27	1.92	0.771	0.018	6.0	11.50	0.893
148	PDDAC, 0.5	15.7	1.80	0.137	3.11	0.422	117	6.1	3.8	0.24	0.89	0.104	0.10	0.82	7.47	0.527
149	PDDAC, 1.0	15.1	1.87	0.068	3.03	0.344	121	7.0	3.7	0.03	0.92	0.133	0.012	1.05	7.30	0.525
150	PDDAC, 0.5; PSFA, 0.2	15.5	1.91	0.064	3.36	0.335	118	7.7	4.0	0.27	0.94	0.179	0.009	1.41	7.67	0.503
151	PDDAC, 0.5; PSFA, 0.5	15.2	2.57	0.156	5.14	0.482	139	5.7	4.5	0.20	1.27	0.353	0.015	2.78	8.97	0.627
152	PDDAC, 1.0; PSFA, 0.2	14.9	2.00	0.070	3.53	0.539	148	10.1	3.8	0.40	0.99	0.115	0.009	0.91	8.10	0.521
153	PDDAC, 1.0; PSFA, 0.5	15.6	2.00	0.086	3.69	0.113	119	5.0	4.2	0.16	0.99	0.177	0.008	1.39	7.77	0.571
154	PDDAC, 0.5; PAA, 0.2	15.6	2.22	0.176	4.28	0.361	131	11.7	4.3	0.23	1.10	0.128	0.009	1.00	8.62	0.635
155	PDDAC, 0.5; PAA, 0.5	15.1	2.51	0.207	4.72	0.561	131	8.6	4.7	0.28	1.24	0.087	0.006	0.68	8.62	0.487
156	PEI, 1.0, PAA, 0.2	15.0	2.89	0.285	6.73	0.615	151	7.5	4.9	0.23	1.54	0.599	0.064	4.6	9.14	1.051
157	PDDAC, 0.2, PAA, 0.2	15.1	2.36	0.171	4.46	0.306	135	9.7	4.3	0.20	1.26	0.111	0.011	0.86	7.54	0.774
158	PDDAC, 0.5, PAA, 0.2	14.9	2.31	0.098	4.47	0.255	127	5.2	4.4	0.13	1.23	1.23	0.006	0.95	7.35	0.79
159	PDDAC, 0.5, PAA, 0.5	15.2	2.55	0.171	5.41	0.322	146	8.9	4.6	0.14	1.36	0.110	0.010	0.85	8.44	0.708

Table 16 (Continued). Strength properties and bonding mechanisms. (Once-dried and classified softwood unbleached kraft.)

Set No.	Additives, % based on fiber	Moist STFI Compressive Strength, lb f/inch		Moist Compressive Strength Factor	Diffuse Reflectance Absorbance Peaks occurring at		Comments
		Av.	SD		1740 (Ester)	1650 (Amide) AI740/AI650	
47	Blank controls	2.89	0.208	1.00	--	--	--
48	PAE, 1.0	3.01	0.490	1.04	0.573	2.00	0.287 Band in ester range 1767-1696 cm <sup>-1</sup>
49	PAE, 1.5	3.02	0.291	1.04	--	--	--
50	PAE, 1.0; CMC, 0.4	3.75	0.326	1.30	-- <sup>a</sup>	-- <sup>a</sup>	--
51	PAE, 1.0; PAA, 0.2	3.41	0.388	1.18	-- <sup>a</sup>	-- <sup>a</sup>	--
146	PEI, 1.0	3.79	0.324	1.31	--	--	--
147	PEI, 1.0; PAA, 0.2	4.10	0.512	1.42	--	--	--
148	PDDAC	3.10	0.282	1.07	--	--	No evidence of ester formation; broad band at 1740-1516 cm <sup>-1</sup>
149	PDDAC	2.96	0.238	1.02	--	--	No evidence of ester formation; broad band at 1740-1516 cm <sup>-1</sup>
150	PDDAC, 0.5; PSFA, 0.2	3.21	0.183	1.11	--	--	No evidence of ester formation; broad band at 1740-1516 cm <sup>-1</sup>
151	PDDAC, 0.5; PSFA, 0.5	3.62	0.321	1.25	--	--	No evidence of ester formation; broad band at 1740-1516 cm <sup>-1</sup>
152	PDDAC, 1.0; PSFA, 0.2	3.33	0.232	1.15	--	--	No evidence of ester formation; broad band at 1740-1516 cm <sup>-1</sup>
153	PDDAC, 1.0; PSFA, 0.5	3.62	0.302	1.25	--	--	No evidence of ester formation; broad band at 1740-1516 cm <sup>-1</sup>
154	PDDAC, 0.5; PAA, 0.2	3.23	0.307	1.11	--	--	No evidence of ester formation; Peaks < 1600 cm <sup>-1</sup>
155	PDDAC, 0.5; PAA, 0.5	3.30	0.278	1.14	--	--	No evidence of ester formation; Peaks < 1720 & 1600 cm <sup>-1</sup>
156	PEI, 1.0, PAA, 0.2	3.28	0.354	1.13	--	--	No ester; Peaks at 1723 & 1661 cm <sup>-1</sup>
157	PDDAC, 0.2, PAA, 0.2	2.94	0.249	1.02	--	--	No ester; one peak at 1720 cm <sup>-1</sup>
158	PDDAC, 0.5, PAA, 0.2	2.93	0.295	1.01	--	--	No ester; one peak at 1727 cm <sup>-1</sup>
159	PDDAC, 0.5, PAA, 0.5	3.31	0.166	1.15	--	--	No ester; one peak at 1720 cm <sup>-1</sup>

<sup>a</sup>Previously tested and found to contain covalent (ester) bonds.

Table 17. The effects of externally applied polystyrene on strength properties. (Whole softwood unbleached kraft handsheets.)

Set No.	Treating Agent	Pickup, % based on sheet wt.	Basis Wt., g/m <sup>2</sup>	Apparent Density, g/cc	Breaking Length, km	Dry Strength Properties						
						TEA, kgm/m <sup>2</sup>	Et, kg/cm	Stretch, %	SD			
External Treatments												
160	Toluene control	--	64.8	0.483	5.36	0.348	8.02	1.137	379	12.4	3.3	0.29
161	10% Polystyrene solution in toluene	3.87	59.9	0.459	6.70	0.569	10.5	2.11	414	15.0	3.6	0.44
162	20% Polystyrene solution in toluene	12.02	71.6	0.538	7.08	0.268	13.7	1.46	496	16.8	3.8	0.34
Internal Treatments												
80	Blank control	--	63.9	0.484	5.20	0.196	7.93	0.939	385	6.4	3.3	0.25
81	PAE, 1.0	--	64.7	0.494	6.14	0.322	8.83	1.354	412	10.9	3.2	0.34
82	PAE, 1.5	--	62.8	0.485	6.31	0.268	9.47	0.757	395	16.0	3.5	0.22
83	PAE, 1.0; CMC, 0.4	--	61.8	0.501	7.35	0.085	13.05	0.745	397	15.3	4.3	0.24
84	PAE, 1.0; PAA, 0.2	--	61.2	0.506	6.97	0.280	11.0	1.09	410	6.7	3.8	0.24

Table 17 (Continued). The effects of externally applied polystyrene on strength properties.  
(Whole softwood unbleached kraft handsheets.)

Set No.	Treating Agent	Moist Strength Properties												
		Moisture Content, % (at 91-93% RH)	Breaking Length, km Av. SD	TEA, kgm/m <sup>2</sup> Av. SD	Et, kg/cm Av. SD	Stretch, % Av. SD	Moist Tensile Factor	Breaking Length, km Av. SD	Wet Tensile Factor					
External Treatments														
160	Toluene control	15.3	3.21	0.117	6.60	0.394	151	9.1	5.0	0.26	1.00	0.157	0.008	1.00
161	10% Polystyrene solution in toluene	14.1	4.12	0.160	8.06	0.737	174	5.1	5.1	0.29	1.28	0.631	0.068	4.02
162	20% Polystyrene solution in toluene	11.6	4.94	0.375	12.7	1.67	232	11.2	5.7	0.31	1.54	1.20	0.213	7.64
Internal Treatments														
80	Blank Control	15.3	2.84	0.224	5.52	0.706	141	4.7	4.7	0.37	1.00	0.141	0.010	1.00
81	PAE, 1.0	15.9	4.42	0.277	9.76	1.33	135	7.4	6.0	0.39	1.56	1.81	0.137	9.48
82	PAE, 1.5	15.4	4.48	0.188	8.95	0.429	132	8.6	5.8	0.20	1.58	2.13	0.197	11.15
83	PAE, 1.0; CMC, 0.4	15.3	5.17	0.244	11.39	0.856	140	3.3	6.4	0.20	1.82	2.19	0.090	11.47
84	PAE, 1.0; PAA, 0.2	15.8	4.60	0.152	9.77	0.763	135	11.0	6.2	0.28	1.62	1.91	0.070	10.00

Table 17 (Continued). The effects of externally applied polystyrene on strength properties. (Whole softwood unbleached kraft handsheets.)

Set No.	Treating Agent	Dry STFI Compressive Strength, lb f/inch		Moist STFI Compressive Strength, lb f/inch		Moist Compressive Strength Factor
		Av.	SD	Av.	SD	
External Treatments						
160	Toluene control	8.82	0.567	3.28	0.218	1.00
161	10% Polystyrene solution in toluene	10.27	1.025	5.02	0.467	1.53
162	20% Polystyrene solution in toluene	14.44	1.280	7.31	0.944	2.23
Internal Treatments						
80	Blank control	8.92	0.707	3.97	0.352	1.0
81	PAE, 1.0	10.56	1.280	--	--	--
82	PAE, 1.5	10.54	1.060	4.41	0.476	1.11
83	PAE, 1.0; CMC, 0.4	10.07	0.545	4.37	0.302	1.10
84	PAE, 1.0; PAA, 0.2	10.11	0.875	3.78	0.454	0.95

## DISCUSSION OF RESULTS

Results in Table 1 serve to show differences in chemical composition and some fiber parameters of the pulps used in this part of the program. It becomes evident in examining the data that rather marked differences can be found in the sugar and lignin contents. As would be expected, the high yield pulps (No. 1, 5, and 6) had substantially higher lignin contents. The hemicellulose content varied from 17-22% with TMP containing the highest level and the 49% yield kraft, the lowest level. The individual sugar contents varied considerably, most notably in glucan content. The two mechanical pulps (No. 5 and 6) tended to be lower in xylan content but higher in mannan when compared to unbleached kraft pulps. The bleached softwood kraft had an intermediate hemicellulose content, low xylan, the highest glucan and of course, the lowest lignin content. It is of interest to note that the isolated fines from the softwood TMP differed from the whole pulp in hemicellulose and lignin contents as well as in most of the individual sugar contents.

With respect to CMC/PAE as a bonding agent in whole pulps, it will subsequently be shown that the most responsive pulps were the bleached kraft and the once-dried 46-47% yield southern pine unbleached kraft. Of the classified pulps, the TMP was the most responsive and the CMP, the least responsive. With respect to composition and with one exception (Pulp No. 7), the most responsive pulps contained higher levels of xylan and glucan and lower levels of lignin. Thus, bonding agent effectiveness may be related to pulp composition.

The results in Table 2 and Fig. 1 to 7 show that combining PAE with the anionic polymers, PSFA or sodium alginate, increased strength to the point where the resulting strength equalled or exceeded that of 1.5% of PAE in dry and

wet tensile properties. However, in general, the strength afforded by these anionic/cationic polymer combinations did not match that of CMC/PAE or PAA/PAE. The optimum anionic polymer/PAE ratio was 0.1-0.2 which may reflect an approximate balance in anionic/cationic charge. (Alginates contain one carboxyl group/sugar unit comprised of mannuronic and guluronic acids.) Since the addition level was increased with polymer ratio, the maxima achieved at lower ratios would translate to economic advantages. It may be noted that PAA/PAE was particularly effective in this 57% yield softwood unbleached kraft. In subsequent comparisons, CMC/PAE was generally the more effective polymer combination. Reasons for the high level of effectiveness of PAA/PAE in this pulp are not apparent. Also, the moist compressive strength factors obtained with the reference bonding agents (PAE, CMC/PAE, etc.) were unusually high when compared to the factors obtained with the same additives in other pulps of conventional yield. A spuriously low moist compressive strength in the blank controls could account for these results (refer to Fig. 7).

Other results of interest in Table 2 (Sets 11 and 12) indicate that either dispersed rosin size or synthetic size can be used to produce water resistance in handsheets containing PAA/PAE. However, the dispersed rosin size reduced strength properties, whereas the synthetic size tended to enhance strength in most cases. This may be due to the presence of starch in the synthetic size. Alum greatly reduced the effectiveness of the PAA/PAE system, presumably due an excess of cationic charge and/or destabilization of the polyacrylic acid. (Note: Handsheets containing CMC/PAE were previously found<sup>1</sup> to be readily sized.) Finally, one of the more significant results in Table 2 is that found in Set 2, where increasing wet pressing to produce a sheet density roughly comparable to that obtained through the addition of polymer additives

(Sets 3-8), failed to match the strength properties afforded by the polymer bonding agents.

Moving on to Table 3, we find that addition of pectins, by themselves, had little or no effect on strength properties presumably due to the anionic character of these materials which have 1 to 3 carboxyl groups/4 galactose units in the galacturonan-rhamnose polymer. However, when combined with PAE (Table 4; Fig. 8 to 13) the synergistic effects found previously with other anionic polymers were again evident. This applies to both the citrus fruit and sugar beet pectins, although the fruit pectin was more effective. In general, the fruit pectin/PAE combinations produced several strength properties which equalled or exceeded CMC/PAE or PAA/PAE, depending upon the polymer ratio and addition level. However, somewhat higher addition levels and/or pectin/PAE ratios (0.6-1.0) were required to achieve these advantages and, considering the cost of pectin (>\$3.00/lb), it was not considered feasible to pursue these studies.

Somewhat more practical results are presented in Table 5 and Fig. 14 to 18 using a once dried softwood unbleached kraft pulp. While the anionic starch/PAE combinations did not match the overall performance of CMC/PAE, the anionic potato starch/PAE combination (Set 56) approached or equalled CMC/PAE in most strength properties. This would apply in particular to those properties which are of specific interest to this project, i.e., moist Et and compressive strength (Fig. 17 and 18). These anionic starches contain 1.2 to 1.4% of carboxymethyl groups, which corresponds to a degree of substitution (DS) of only 0.11-0.12 compared to a DS of 0.7 for the CMC and 1.0 for PAA. This may account for the greater amount of potato starch required to improve bonding compared with CMC. However, the reduced response by the anionic cornstarch cannot be explained on that basis.

Subsequent work involved a comparison of the effectiveness of PAE, CMC/PAE, and PAA/PAE in whole and classified pulps differing in type, wood source and yield. The first of those involved a softwood TMP with results in Table 6 and Fig. 19 to 23. Bar graphs (Fig. 19 to 22) show a general trend for lower strength levels in the classified pulp series as might be expected. On the other hand, the lower strength of the blank controls from the classified pulp also results in a greater difference between the controls and sheets containing PAE and the duopolymer systems. In the case of the whole pulp, this manifests itself in generally lower improvements in the presence of the additives. Another effect that becomes evident is the relatively low response to the additives in dry and moist Et and moist compressive strength (Fig. 21 to 23) suggesting that improved interfiber bonding may not be sufficient for high moist Et and compressive strength. Finally, in the case of the softwood TMP, CMC/PAE was consistently more effective than PAA/PAE and the latter, in turn, was more effective than 1.5% PAE in most but not all cases. The duopolymer systems again produced high levels of breaking length, TEA, and stretch, both dry and moist; also wet tensile.

Table 7 and Fig. 24 to 29 compare results for the whole and classified 49% yield softwood unbleached kraft (Pulp No. 3). In agreement with the results from the softwood TMP study, generally higher strength levels were obtained with the whole pulp. Once again, CMC/PAE provided the highest dry and moist breaking lengths, but PAE or PAA/PAE produced the highest Et levels. As previously observed, differences in additive effectiveness were rather slight, particularly in the case of moist Et. Differences in dry compressive strength were more pronounced, due possibly to the age of the samples at the time of testing.

The results in Table 8 compare polymer effectiveness at pH 7 to 9 vs. 4.5 to 5.0. Some slight differences in strength properties are evident. For example, PAA/PAE appears to be more effective in dry strength at pH 4.5 but this does not apply to moist and wet strength properties, excluding compressive strength. It was expected that PAA/PAE might prove consistently more effective at low pH, since PAA is quite acidic and would be substantially in the nonionized form at pH 4.5. Under this condition, the polyacrylic acid should be more amenable to ester formation. Results with CMC/PAE were also inconsistent with respect to pH. In that case, higher dry and moist tensile strength was produced at pH 7 to 9.

A comparison of whole and classified pulps from the once-dried softwood unbleached kraft are presented in Table 9 and in Fig. 30 to 35. In this case, as in the previous two, the whole pulp tended to produce higher strength. Et (Fig. 32 to 33) again showed a low response to the polymeric bonding agents, particularly in whole pulp. Greater differences are evident in dry and moist compressive strength (Fig. 34-35). It is of interest to note that treating the classified pulp with CMC/PAE produced strength properties which in most cases roughly equalled those of the whole pulp containing the same polymers. This applies to several pulps utilized in the program.

The next comparison of whole and classified pulps involved a spruce chemimechanical pulp, and the results are presented in Table 10 and Fig. 36 to 41. In general, the trends in strength properties follow those of the previous pulps. Greater improvements in strength properties occurred in the classified pulp as reflected in the moist and wet tensile and moist compressive strength factors. It is of interest to note that the CMP had dry tensile strengths in the whole and classified conditions equal to those of the average yield, once-dried unbleached kraft. On the other hand, percentage increases due to CMC/PAE

were slightly lower in the CMP. The final comparison of polymer additive response involved the softwood bleached kraft (Pulp No. 7). Results for this series are presented in Table 11 and Fig. 42 to 49. Setting aside Sets 105 to 108 temporarily, we find that the bleached kraft pulp responded to the bonding agents in about the same manner as the preceding pulps. Actually, the response of the whole bleached kraft pulp to CMC/PAE was the highest of all pulps insofar as dry tensile is concerned, while the increase in the classified pulp was comparable to the average yield unbleached kraft pulps. No attempts will be made to interpret the brightness data, since these tests were made several weeks after the handsheets had been prepared and are, therefore, subject to error.

Sets 105 to 108 and Fig. 48 and 49 show the effects of blending carboxymethylated fiber with the bleached kraft pulp at addition levels ranging from 0.04% (Set 105) to 10% in Set 108. This represents an interesting series, since the CMC is part of the fiber fraction and was not added externally. However, upon comparing results obtained with internal addition vs. external addition (Sets 103 and 105) and Fig. 48 and 49, it becomes evident that having the CMC present in fibrous form is notably less effective than external addition. Diffuse reflectance FTIR analysis of Sets 103 and 105 (Table 11) indicates that a higher level of ester formation occurred with external addition. Conceivably, the carboxyl groups in the blended pulps are less accessible for covalent bonding compared with external addition. These results lend some support for the concept of homocrosslinking in Sets 105 to 108 as described by Westfelt<sup>3</sup>.

The foregoing series (Unit 2) provided a comparison of bonding agent effectiveness in whole and classified pulps, and it is concluded from this unit that the presence of fines reduces the effectiveness of the bonding agents in most

cases. That is, greater improvements in strength relative to the blank or PAE controls are achieved in classified pulps. Conceivably, the fines fraction adsorbs a disproportionate amount of the bonding agent, thereby masking its effectiveness. Another conclusion to be drawn from this unit is that the bonding agents are generally more effective in improving breaking length than Et suggesting that the polymers improve interfiber bonding but have a notably reduced effect on bulk properties.

The next unit considers the effect of fines on strength properties both in the absence and presence of bonding agents. Two pulps were utilized in this work: a high yield softwood TMP (Pulp No. 5) and an average yield softwood unbleached kraft (Pulp No. 4). Results for the TMP (Table 12 and Fig. 50 and 51) show that readdition of isolated fines to the classified pulp produced dry and moist strength properties which were equal to, or greater than, those of the whole pulp, provided that the moist strength properties were measured at a moisture content of 15 to 16% or 88 to 89% R.H. This moisture level is roughly comparable to that encountered with the kraft pulp conditioned at 91 to 93% R.H. Addition of double the normal level of fines greatly increased moist strength properties but failed to reach the level afforded by the polymer bonding agents. Other noteworthy effects in Table 12 include the following:

1. CMC/PAE proved generally superior to PAA/PAE
2. Addition of CMC/PAE to the classified fiber was generally more effective than to the fines fraction treated separately,
3. With a few exceptions, combining treated classified fibers and fines to form a whole pulp produced higher dry, moist, and wet strength than adding the bonding agents directly to the original whole pulp.

4. Treating the long fiber fraction with 1.4% of CMC/PAE was generally equivalent to, or superior to, the addition of 60% of untreated fines.

A parallel fines-additive study was carried out with the once-dried unbleached softwood kraft (Pulp No. 4) and the results are recorded in Table 13 and Fig. 52 and 53. In contrast to the TMP study, readdition of fines equal to the level contained in the whole pulp (12%) failed to match the original whole pulp in dry and moist strength properties. However, like the TMP, maximum strength was generally obtained when the bonding agents were added to the long fiber fraction or to both the long fiber fraction and fines fraction in proportion to their weight. In this case, CMC/PAE and PAA/PAE were more effective than PAE in both the classified and whole pulps.

Thus, it may be concluded from the fines-additive study that the most effective use of polymer bonding agents involves addition to the long fiber fraction rather than to the fines fraction. These results conform to the previous unit which showed that, in most cases, greater increases in strength, relative to the controls, were achieved when the bonding agents were added to the classified pulps.

Results obtained in studies of bonding mechanisms are presented in Tables 14-16. The data in Table 14 show clear evidence of covalent bonding with CMC/PAE and PAA/PAE in a variety of pulps. While limited in scope, the data in Table 15 reveal several noteworthy effects.

First of all, neither PEI nor cellulose can react with PSFA to form a covalent bond but, theoretically, PAA could react with cellulose to form an ester (covalent bond). Of course, it was previously established in Progress

Report One and Table 14 of this report that CMC/PAE reacts either with itself or cellulose to form ester bonds. However, the analytical data in Table 15 show no evidence of ester formation with PEI, PEI/PSFA, and PEI/PAA. In spite of this, rather substantial strength improvements were obtained in Sets 143 to 145 and, in particular, Set 145, which proved about as effective as PAE. PAE is capable of forming ester linkages as shown in Table 16. If it is assumed that the relatively high strength developed in Set 145 was due to ionic bonding (in keeping with the relatively low wet tensile factors) then it may be concluded that ionic bonding may be about as effective as covalent bonding in producing dry and moist strength properties. Of course, the highest overall strength levels occurred in Set 142, where covalent bonding is known to occur.

The results in Table 16 indicate that covalent bonding occurred only in Set 48 (1% PAE). Of course, previous evidence indicated that covalent bonding also exists in the CMC/PAE and PAA/PAE systems (Sets 50 and 51). Once again, rather substantial increases in strength over the blank controls were obtained in the absence of covalent bonding as in Sets 146, 147, 151, 156, and 159. Some of these are the same as those in Table 15. Neither PDDAC nor PSFA can form covalent bonds with cellulose, but when PDDAC was combined with either PAA or PSFA moderate strength increases were obtained, presumably due to ionic bonding. Of interest are the high moist compressive strength factors achieved with PEI and PEI/PAA (Sets 146 and 147). These moist compressive strengths were among the highest levels achieved to date by the internal addition procedure. Also, wet tensile factors for these ionically bonded papers suggest better repulpability than covalently bonded papers. But aside from the strength increases afforded by PEI, PEI/PAA and several PDDAC combinations, the overall strength levels attained fall short of those produced by CMC/PAE. On the other hand, PEI and

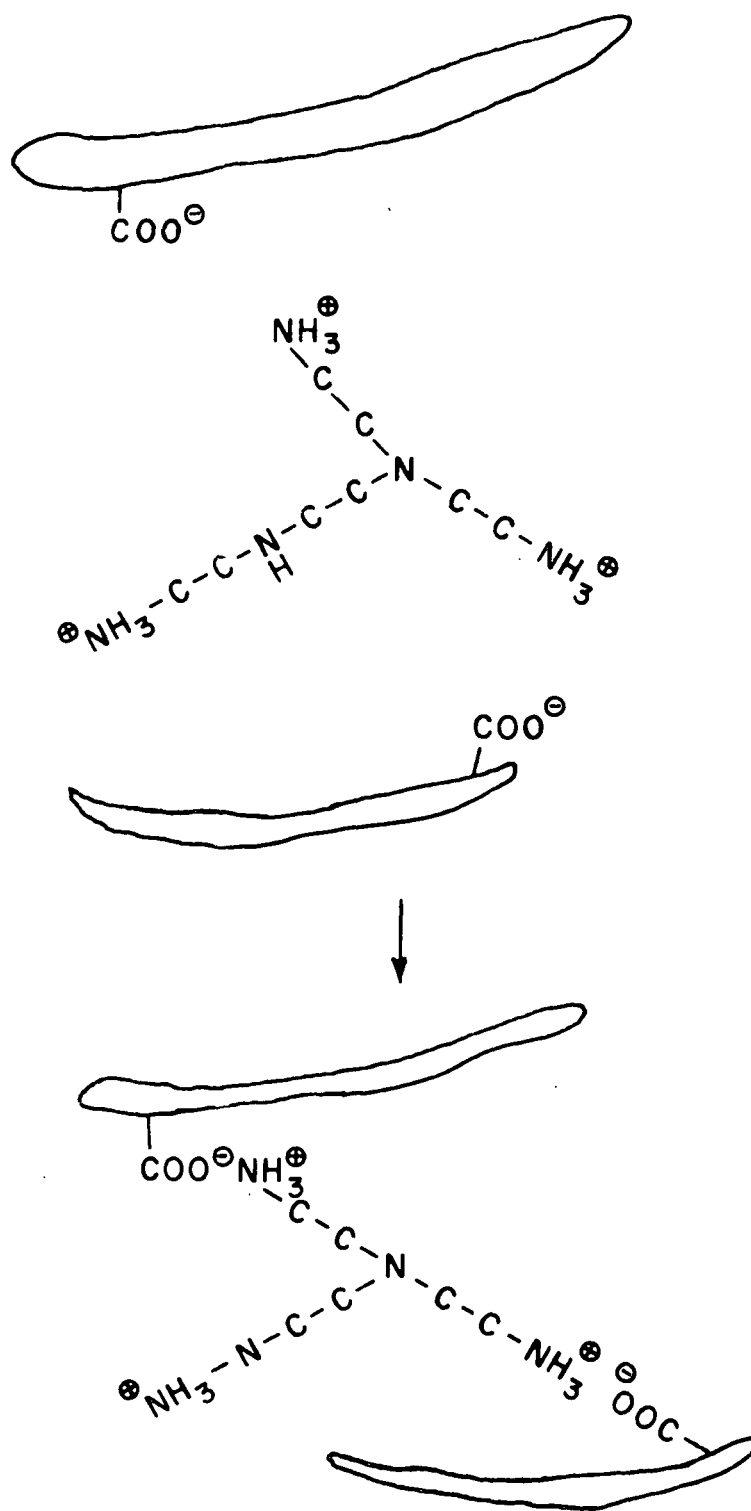


Figure 54. Ionic bonding - PEI + cellulose.

PEI/PAA compare favorably with PAA/PAE and PAE in most cases and particularly in Et and compressive strength. Thus, these presumably ionic bonded systems show potential for improving the strength properties of paper and board, which are of specific interest to this project. A schematic representing ionic bonding between PEI and cellulose fibers is presented in Fig. 54.

External treatment of whole softwood unbleached kraft handsheets with toluene solutions of polystyrene (Table 17) produced rather interesting results, although of limited practical value at this point. As might be expected, application of a material with a high modulus provided a high level of Et and compressive strength at an add-on level of 12%. The moist compressive strength factor with polystyrene was 2.2 (Set 162) compared with 1.1 for 1.5% PAE and 1% PAE/0.4% CMC. (Sets 82 and 83). Surprisingly, application of polystyrene also produced levels of breaking length, TEA, and stretch which were roughly comparable to the internal addition of CMC/PAE. Conceivably, some polystyrene may have penetrated the cell wall under the conditions of these tests and thereby contributed to strength and moisture resistance. It should be noted that the moisture contents of the polystyrene-treated papers were notably lower than those of the internal addition references (Sets 81 to 84). This, in itself would assist moist strength properties. In any case, some potential for external treatments is indicated.

## REVIEW

In brief review, several anionic polymer/PAE combinations produced strength properties approaching or equalling those of the "standard" CMC/PAE and PAA/PAE combinations. Of these, carboxymethylated potato starch/PAE appears to offer the best balance of strength and economic feasibility. While CMPS/PAE produced slightly lower breaking lengths than CMC/PAE, it tended to produce higher moist Et and compressive strengths. In most cases, the polymer additives and combinations were found to be more effective in improving strength in classified pulps compared to the whole (unclassified) pulps. This was supported in fines-bonding agent studies utilizing two widely differing pulps. In general, the results indicate that superior strength can be achieved by adding the bonding agents to the long fiber fraction rather than to the fines. A softwood TMP proved more sensitive to the presence of fines than a softwood unbleached kraft pulp. The bonding agents were more effective in improving breaking length or interfiber bonding than in enhancing fiber stiffness or bulk properties.

Analysis of polymer-bonded papers using diffuse reflectance FTIR indicates that substantial improvements in strength over the blank controls can be achieved in the absence of covalent (ester) bonds. Presumably, ionic bonds along with hydrogen bonds occur in these systems. In some cases, these ionic bonds were found to provide higher levels of moist Et and STFI compressive strength but lower wet tensiles than were afforded by the covalently bonded systems. The lower wet tensiles would be expected to translate to improved repulpability. Overall, however, higher strength levels were generally attained in covalently bonded papers. Finally, the external application of polystyrene to unbleached softwood kraft handsheets was found to provide high levels of Et and compressive

strength while maintaining tensile and TEA levels roughly comparable to those achieved by the internal addition of PAE or CMC/PAE. Further consideration will be given to this approach in future work programs.

## FUTURE WORK

While covalently bonded fiber networks, as exemplified by CMC/PAE, continue to demonstrate the highest overall strength properties in a wide range of pulps, it now appears that high moist Et and STFI compressive strength can be achieved in the absence of covalent bonding, i.e., in the presence of ionic bonding. Future work will pursue these systems in order to provide a viable alternative to the covalently bonded papers which are difficult to repulp. This work will not detract from the continued pursuit of new bonding agents, in particular, materials which could replace PAE as the cationic component in duopolymer systems. Means will also be sought to improve the efficiency of polymer bonding agents in whole (fines containing) pulps. The study of bonding mechanisms through chemical analysis will be continued in an effort to differentiate between polymer-to-polymer bonds and polymer-to-fiber bonds. Finally, consideration will be given to external treatments which would be more amenable to practical mill operations than the solvent applications described in this report.

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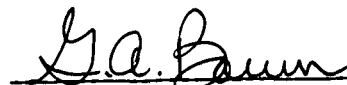
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