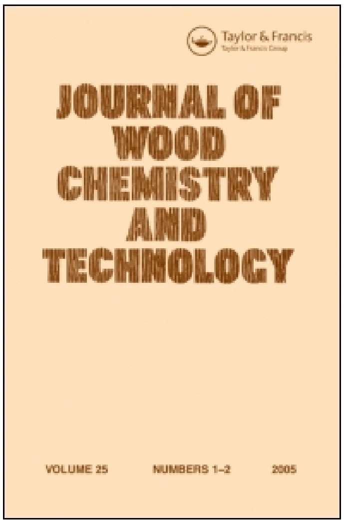

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GRAFT POLYMERIZATION OF VINYL MONOMERS ON PEROXIDIZED CELLULOSIC FIBERS

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ABSTRACT

Bleached kraft softwood pulp was sequentially oxidized with ruthenium tetroxide, peroxidized with hydrogen peroxide and then grafted with acrylamide or acrylonitrile monomers in the presence of ferrous ions. Good polymer loadings and grafting efficiencies were obtained. It was found that hot pressed dry paper sheet properties could be improved by a small addition of polyacrylamide-grafted pulp.

INTRODUCTION

The methods for grafting vinyl polymers on cellulosic fibers which give the highest yields and grafting efficiencies involve redox initiation reactions and free radical polymerization. The grafting efficiency is a direct result of the formation of free radicals on the cellulosic surface and the minimization of the radical transfer.[1] One of the methods for generating free radical sites on cellulose is by decomposing peroxide groups introduced into the substrate.

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The formation of hydroperoxide groups on cellulose surfaces by irradiation[2] or by ozonation[3] has been known for long a time. However, these methods can result in cleavage of the cellulose macromolecules, thereby causing a weakenning of the fibers.

A method for introducing peroxide groups into cellulose without excessive degradation is treatment with hydrogen peroxide in acidic medium.[4,5]

Kubota and Ogiwara showed that peroxide groups formed by reaction of cellulose fibers with hydrogen peroxide could bu used as active sites for free radical copolymerization with vinyl monomers.[6] The active sites were formed either by thermal decomposition of the hydroperoxides or by reaction with ferrous ions.[7] In the present work, the peroxide groups attached to the cellulose backbone were produced by a sequential reaction of the cellulose with ruthenium tetroxide and then hydrogen peroxide. In this paper we report a study of the effects of different parameters on the grafting reaction for a bleached kraft pulp, and the effect of grafted polymers on paper properties.

EXPERIMENTAL

Materials.

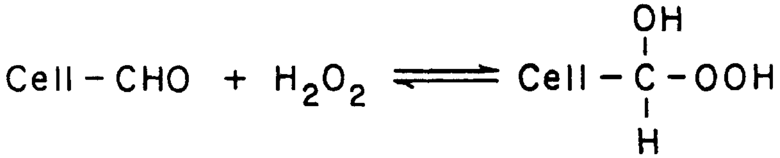
Bleached kraft pulp (lignin content ; 0.01%) was used as the grafting substrate.

Ruthenium tetroxide was formed by adding catalytic quantities of ruthenium trichloride (1 mg/g of pulp) to an aqueous solution of NaOCl (0.5% of Cl_2).[8]

Acrylonitrile was purified by distillation, the middle fraction was stored in dark bottles at 4°C. All other chemicals employed were used such as supplied.

Pulp peroxidation

Cellulose peroxide was formed by treatment of the oxidized pulp (10 g) with a mixture of 40 mL of concentrated sulfuric acid and 200 mL of hydrogen peroxide (35%) at 25°C for 60 min.[7,10] After peroxidation the pulp was generously washed with distilled water at 4°C. According to the reaction mechanism proposed by Kubota and Ogiwara, the reactions between oxidized cellulose and hydrogen peroxide are as follows:



$$\text{Cell-CHO} + H_2O_2 \rightleftharpoons \text{Cell}-\underset{\substack{|\\ H}}{\overset{\substack{OH\\ |}}{C}}-\text{OOH}$$

α- hydroxyhydroperoxide

$$\text{Cell-COOH} + H_2O_2 \rightleftharpoons \text{Cell-CO}_3\text{H} + H_2O$$

The peroxide content of the pulp was determined by the iodometric titration method.[11]

Grafting.

Radicals were generated on fiber surfaces by reaction with ferrous ions.

Dry peroxidized pulp (10 g) was mixed with 50 mL of distilled water, 2 g of surfactant (Tween 80) and 10 g of vinyl monomer. After a 15 min presoak, 350 mL of ferrous ammonium sulfate solution (1-3M) was added, the pH adjusted to 5 (with 0.1 N H_2SO_4) and the start of copolymerization recorded. The mixture was stirred gently and the temperature was controlled at 25 ± 0.5°C. After the desired time, the resulting polymerization mixture was filtered and washed with an excess of water, and the polymerized pulps was dried at 50°C for 48 h. The reaction scheme is shown in Figure 1.

Determination of the grafting parameters.

The removal of the homopolymer absorbed onto the grafted pulp was achieved by Soxhlet extraction with the appropriate solvent (dimethylformamide for polyacrylonitrile, and water for polyacrylamide). Grafting parameters were defined as follows:

Polymer loading, (%) : ((A - B)/((B)) X 100

Grafting efficiency, (%) : ((A - B)/(D - B)) X 100

Degree of conversion
(Polymerization yield)(%): ((D - B)/(C)) X 100

Where A is weight of product after copolymerization and extraction, B is weight of pulp, C is weight of monomer charged, and D is weight of products after copolymerization.

Testing.

Handsheets were prepared and tested according to TAPPI standard's (T205, T220, T231) and then pressed with 50 Kg/cm^2 at 150°C for 60 s.

RESULTS AND DISCUSSIONS

Many methods of grafting on pulp are of theoretical interest but are not used industrially. Nevertheless, the most interesting processes are those based on radical polymerization. In this context the redox systems are particularly relevant due to the fact that water is the suspension medium. One of the more promising methods for grafting synthetic polymers onto oxidized cellulose is based on an ion-exchange reaction, whereby a ferrous ion is in-

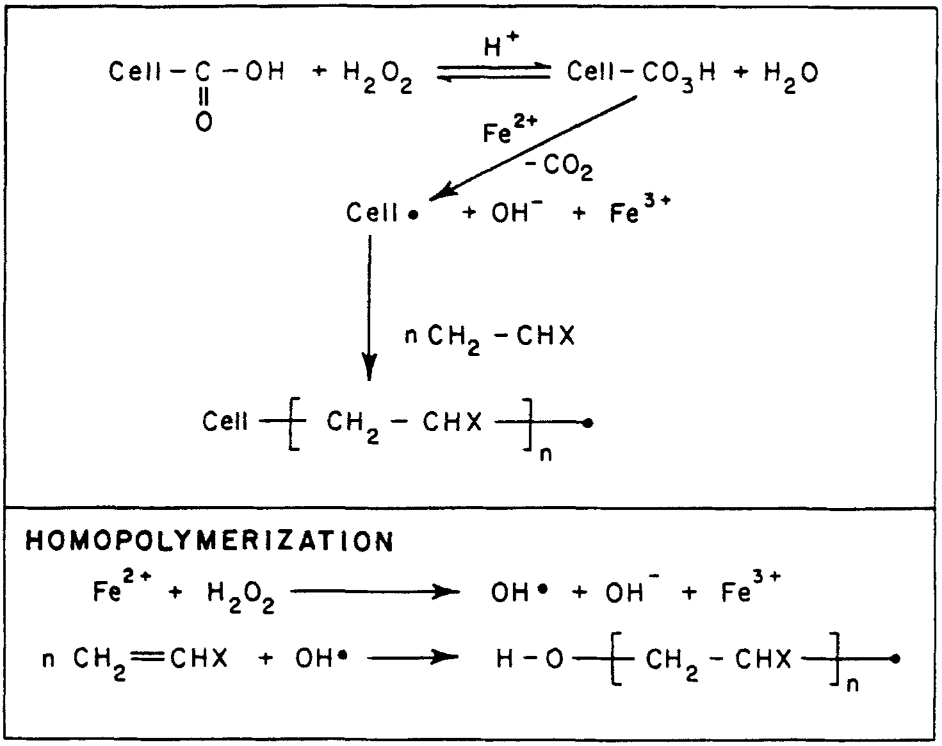


Figure 1. ACTIVATION OF CELLULOSE PEROXIDE BY FERROUS ION AND POLYMERIZATION.

troduced on all carboxylic groups.[11] This work concerns fibers modified by graft copolymerization of acrylonitrile and acrylamide initiated by decomposition of peroxide groups generated on the cellulose through successive oxidation with ruthenium tetroxide[8] and hydrogen peroxide.[6,7,10]

In some systems, the rate of radical generation is a function of the pH of the reaction mixture.[13] The effect of pH in our system is shown in Table 1. It can be concluded that the preferred pH range is 5-7 as far as both the grafting efficiency and the polymerization yield are concerned. It is worth noting that this range is also the most favorable for the maximum absorption of ferrous ions onto the functional groups.[14]

In the work of Kubota and Ogiwara,[6,7,10] decomposition of peroxide groups was achieved by the combined action of ferrous ions and heating. We have verified that thermal decomposition of the peroxide in aqueous media at 60°C is not sufficient to initiate effective grafting when ferrous ions are absent (Table 2).

The effect of the ferrous ion concentration on grafting parameters is shown in Table 2 and in Figure 2. The initial sharp increase in both grafting efficiency and conversion is followed by a levelling at a ferrous ion concentration of 0.25 mmol/litre.

The results presented in Table 3 reflect the dependence of grafting on reaction time. It is seen that a rapid polymerization takes place during the first 15 minutes of the reaction; the rate then decreases, and after about 30 minutes of reaction the system is no longer active.

The results presented in Table 4 reflect the influence of the temperature on grafting. In the case of acrylonitrile both the polymerization yield and the grafting efficiency increase with temperature. It must be emphasized that we obtained polymer loading of 122% at 60°C in the case of graft polymerization of acrylamide, while Hatakeyama and co-workers[15] obtained only 65% loading using ground wood pulp in grafting initiated by an acetic acid-hydrogen peroxide process[15]. Table 5 shows the effects of peroxidation of the pulp on the polymerization yield and grafting efficiency. The results also show the effect of the monomer concentration on the grafting parameters. For acrylamide an increase in the pulp to monomer ratio enhanced the polymerization yield. The levelling-off of the grafting efficiency near 80% may be due to a constant monomer transfer rate. When acrylonitrile was used, the polymerization yield and grafting efficiency behaved similarly, which shows the complexity of the chain transfer mechanism. This is probably due to the heterogeneous double nature of the system,

TABLE 1

EFFECT OF INITIAL pH ON GRAFTING

pH	Polymer loading (%)	Grafting efficiency (%)	Degree of conversion (%)
3	99	76	65
5	122	81	75
6	121	81	75
7	112	76	74
8	92	59	76

Reaction conditions: Cellulose peroxide, 10.0 g (oven-dry weight); monomer (acrylamide), 20.0; temperature, 60°C; water, 200 ml; Fe^{2+} = 1.0 mmol/l; reaction time, 90 min.

TABLE 2

DEPENDENCE OF GRAFTING ON CONCENTRATION OF Fe^{2+}

Fe^{2+} mmol/l	pH	Grafting ratio, %	Grafting efficiency, %	Polymerization yield, %
0.00	5.0	2	22	5
0.05	5.0	16	67	12
0.25	5.0	114	80	71
0.50	5.0	120	80	75
1.00	5.0	121	81	75

Reaction conditions: Cellulose peroxide, 10.0 g (oven-dry weight); monomer (acrylamide), 20.0 g; temperature, 60°C; water, 200 ml; reaction time, 90 min.

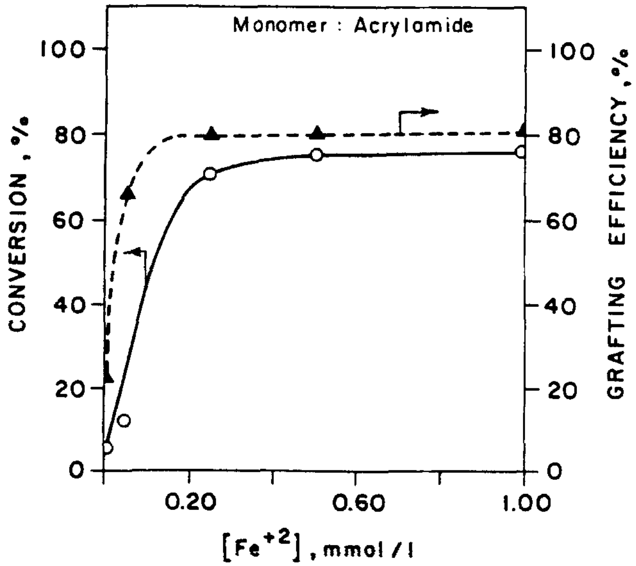


Figure 2. DEPENDANCE OF GRAFTING PARAMETERS ON THE FERROUS ION CONCENTRATION.

consisting of acrylonitrile in water and water in acrylonitrile, a homopolymerization initiated by a water soluble redox systems proceeds only in the aquous solution of acrylonitrile. We have not tried to clarify this point.

Previous work in our laboratory[16,19], as well as other studies[20,21] has clearly demonstrated the potential of the "xanthate" method for grafting vinyl monomers with excellent results on industrial pulps. A comparaison of the xanthate and hydroperoxide methods is presented in Table 6. We can see that while the xanthate method gives better results with acrylonitrile, the reverse is true with acrylamide.

It was shown that the properties of grafted fibers vary with the nature, the length of the grafted chains and the grafting ratio.[22] In the present work, handsheets were prepared and tested according

TABLE 3

DEPENDENCE OF GRAFTING ON REACTION TIME

Time min.	pH	Grafting ratio, %	Grafting efficiency, %	Polymerization yield, %
15	5.0	99	73	68
30	5.0	117	78	75
60	5.0	120	80	75
90	5.0	122	81	75

Reaction conditions: Cellulose peroxide, 10.0 g (oven-dry weight); monomer (acrylamide), 20.0 g; temperature, 60°C; water, 200 ml; Fe^{2+} = 1.0 mmol/l.

TABLE 4

EFFECT OC TEMPERATURE ON GRAFTING

Monomer	Temperature °C	Grafting ratio, %	Grafting efficiency, %	Polymerization yield, %
Acrylamide	25	135	88	77
	60	122	81	75
	85	111	74	75
Acrylonitrile	25	111	79	70
	60	144	80	90
	85	140	81	81

Reaction conditions: Cellulose peroxide, 10.0 g (oven-dry weight); monomer (acrylamide), 20.0 g; water, 200 ml: Fe^{2+} = 1.0 mmol/l; reaction time, 90 min.

TABLE 5

EFFECT OF MONOMER CONCENTRATION ON GRAFTING

Pulp	Monomer g.		Grafting ratio, %	Grafting efficiency, %	Polymerization yield, %
Bleached soft-wood kraft, pulp	Acrylamide	20.0	2	51	2
Bleached soft-wood kraft pulp oxidized		20.0	121	81	75
		10.0	63	81	78
		5.0	32	80	80
Bleached soft-wood kraft, pulp	Acrylonitrile	20.0	12	85	7
Bleached soft-wood kraft pulp oxidized		20.0	141	80	88
		10.0	72	80	90
		5.0	75	83	91
		2.5	22	88	99

Reaction conditions: Cellulose peroxide, 10.0 g (oven-dry weight); temperature, 60°C; water, 200 ml; Fe^{2+} = 1.0 mmol/l.

TABLE 6

COMPARISON OF THE GRAFTING METHODS

Grafting method	Monomer	Fe^{2+}	Grafting ratio, %	Grafting efficiency, %	Polymerization yield, %
Peroxide	Acrylamide	1.0 mmol/l	135	88	77
Xanthate	Acrylamide	0.004 %	47	65	36
Peroxide	Acrylonitrile	1.0 mmol/l	111	79	70
Xanthate	Acrylonitrile	0.004 %	175	85	97

Reaction conditions: Peroxide method: Cellulose peroxide, 10.0 g (oven-dry weight); temperature, 25°C; water, 200 ml; monomer, 20 g; reaction time, 90 min.; initial pH = 5.0

Xanthate method[13].

TABLE 7

PAPER PROPERTIES OF GRAFTED BLEACHED SOFTWOOD KRAFT PULP (BSKP)

TESTS SAMPLES	BULK cc/g		BREAKING LENGTH AIR DRIED, km		BREAKING LENGTH WET, km	
	S	P	S	P	S	P
BLEACHED SOFTWOOD KRAFT PULP	1.64	1.54	5.56	5.29	0.92	0.69
BLEACHED SOFTWOOD KRAFT PULP OXIDIZED	1.51	1.40	3.87	3.02	0.70	0.53
BSKP * ACRYLAMIDE Loading: 122%	3.05	2.90	3.80	4.00	0	0.60
BSKP * ACRYLAMIDE Loading: 63%	2.53	2.36	3.84	4.10	0.20	0.30
BSKP / (BSKP * AM) Ratio: 1/1 Loading: 122%	2.32	2.17	4.06	4.59	0.58	0.68
BSKP / (BSKP * AM) Ratio: 1/1 Loading: 63%	2.16	2.00	3.92	4.47	0.53	0.65
BSKP / (BSKP * AM) Ratio: 4/1 Loading: 122%	2.03	1.78	5.18	5.60	0.89	0.90
BSKP / (BSKP * AM) Ratio: 4/1 Loading: 63%	1.91	1.70	5.65	6.2	0.84	0.94
BSKP * ACRYLONITRILE Loading: 140%	0	3.26	0	0.80	0	0.41
BSKP * ACRYLONITRILE Loading: 72%	6.50	2.81	0	0.90	0	0.35
BSKP / (BSKP * ACN) Ratio: 1/1 Loading: 140%	4.16	2.26	0.76	1.97	0.03	0.45
BSKP / (BSKP * ACN) Ratio: 1/1 Loading: 72%	4.10	2.12	0.87	2.14	0.05	0.47
BSKP / (BSKP * ACN) Ratio: 4/1 Loading: 140%	2.78	1.93	2.27	3.83	0.08	0.59
BSKP / (BSKP * ACN) Ratio: 4/1 Loading: 72%	2.67	1.89	2.48	4.03	0.11	0.74

S : Sheets prepared by standard procedure.
P : Sheets prepared by standard procedure but pressed with: 50 kg/cm^2 at 150°C.
Pressing time: 60 sec.

TABLE 8

PAPER PROPERTIES OF GRAFTED BLEACHED SOFTWOOD KRAFT PULP (BSKP)

TESTS / SAMPLES	TEAR FACTOR mN·m^2/g		BREAKING LENGTH ZERO SPAN AIR DRIED, km		BREAKING LENGTH ZERO SPAN WET, km	
	S	P	S	P	S	P
BLEACHED SOFTWOOD KRAFT PULP	16.4	10.1	12.70	12.20	10.30	7.80
BLEACHED SOFTWOOD KRAFT PULP OXIDIZED	1.4	1.2	5.90	4.90	2.58	1.80
BSKP • ACRYLAMIDE Loading: 122%	1.6	1.8	6.00	6.20	0	2.12
BSKP • ACRYLAMIDE Loading: 63%	1.5	1.8	6.14	6.80	1.97	2.43
BSKP / (BSKP * AM) Ratio: 1/1 Loading: 122%	9.4	9.4	8.20	9.50	3.28	6.48
BSKP / (BSKP * AM) Ratio: 1/1 Loading: 63%	11.3	11.8	8.00	9.50	5.00	7.70
BSKP / (BSKP * AM) Ratio: 4/1 Loading: 122%	14.3	14.8	11.30	13.0	9.53	10.00
BSKP / (BSKP * AM) Ratio: 4/1 Loading: 63%	15.0	15.8	11.90	13.20	9.99	10.36
BSKP * ACRYLONITRILE Loading: 140%	0	2.9	0	3.00	0	2.20
BSKP * ACRYLONITRILE Loading: 72%	0	3.0	0	3.40	0	2.10
BSKP / (BSKP • ACN) Ratio: 1/1 Loading: 140%	9.5	10.9	7.15	8.20	5.40	6.20
BSKP / (BSKP • ACN) Ratio: 1/1 Loading: 72%	10.3	12.0	7.60	9.86	5.79	7.36
BSKP / (BSKP * ACN) Ratio: 4/1 Loading: 140%	16.2	16.4	10.60	11.80	7.16	8.00
BSKP / (BSKP * ACN) Ratio: 4/1 Loading: 72%	16.0	16.8	11.10	12.30	7.92	8.90

S : Sheets prepared by standard procedure.
P : Sheets prepared by standard procedure but pressed with: 50 kg/cm^2 at 150°C.
Pressing time: 60 sec.

TABLE 9

PAPER PROPERTIES OF GRAFTED BLEACHED SOFTWOOD KRAFT PULP (BSKP)

TESTS / SAMPLES	DIMENSIONAL STABILITY %		STRETCH AT BREAK AIR DRIED, %		STRETCH AT BREAK WET, %	
	S	P	S	P	S	P
BLEACHED SOFTWOOD KRAFT PULP	0.50	0.50	3.39	3.20	3.52	3.30
BLEACHED SOFTWOOD KRAFT PULP OXIDIZED	0.60	0.55	0.59	0.46	1.52	1.30
BSKP * ACRYLAMIDE Loading: 122%	2.27	2.45	0.66	0.71	0	4.57
BSKP * ACRYLAMIDE Loading: 63%	1.00	1.20	0.66	0.80	3.88	4.29
BSKP / (BSKP * AM) Ratio: 1/1 Loading: 122%	0.85	0.70	2.00	2.34	4.30	4.78
BSKP / (BSKP * AM) Ratio: 1/1 Loading: 63%	0.70	0.60	1.90	2.29	4.05	4.57
BSKP / (BSKP * AM) Ratio: 4/1 Loading: 122%	0.45	0.50	3.51	3.86	4.15	4.60
BSKP / (BSKP * AM) Ratio: 4/1 Loading: 63%	0.45	0.50	3.20	3.48	3.94	4.20
BSKP * ACRYLONITRILE Loading: 140%	0	1.85	0	0.56	0	1.05
BSKP * ACRYLONITRILE Loading: 72%	0.80	1.50	0	0.52	0	1.00
BSKP * ACRYLONITRILE Ratio: 1/1 Loading: 140%	0.80	0.70	1.83	2.00	2.49	3.86
BSKP / (BSKP * ACN) Ratio: 1/1 Loading: 72%	0.70	0.60	1.93	2.06	2.81	3.92
BSKP / (BSKP * ACN) Ratio: 4/1 Loading: 140%	0.55	0.50	2.26	2.90	3.26	4.53
BSKP / (BSKP * ACN) Ratio: 4/1 Loading: 72%	0.55	0.50	2.51	3.30	3.85	4.91

S : Sheets prepared by standard procedure.
P : Sheets prepared by standard procedure but pressed with: 50 kg/cm2 at 150°C.
Pressing time: 60 sec.

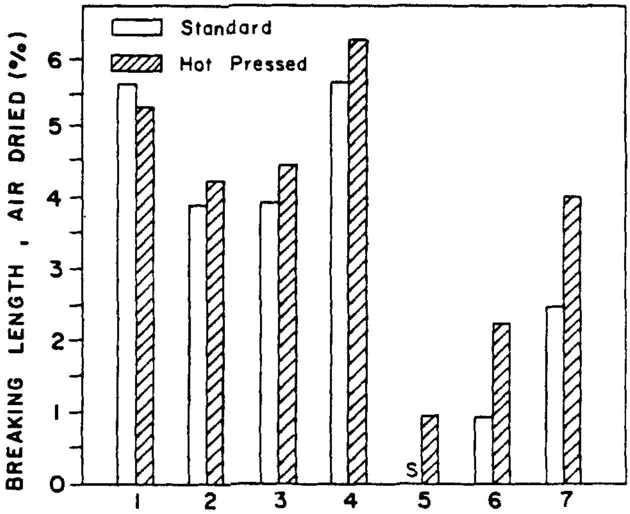


Figure 3. DRY BREAKING LENGTH OF SHEETS FROM THE UNGRAFTED AND VINYL POLYMER GRAFTED CHEMICAL PULP.

1) Bleached softwood kraft pulp (BSKP)
2) BSKP -grafted with acrylamide, loading 63
3) BSKP + BSKP -grafted with acrylamide, loading 63
Ratio pulp/pulp grafted: 1/1
4) BSKP + BSKP -grafted with acrylamide, loading 63
Ratio pulp/pulp grafted: 4/1
5) BSKP -grafted with acrylonitrile, loading 72
6) BSKP + BSKP -grafted with acrylonitrile, loading 72
Ratio pulp/pulp grafted: 1/1
7) BSKP + BSKP -grafted with acrylonitrile, loading 72
Ratio pulp/pulp grafted: 4/1

S: Sheet not consistent

to TAPPI standards. In some cases the standard preparation was followed by hot pressing.[24] The pulp composition was varied from 0 to 100% of grafted pulp. The effects of grafted pulp addition on the paper properties are summarized in Table 7 to 9.

Significant effects on the mechanical properties of the paper which are clearly due to the chemical treatment of the fibers were observed.

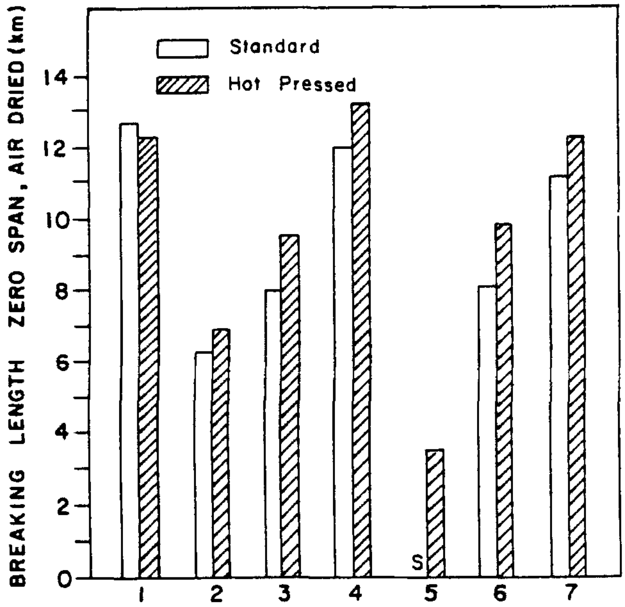


Figure 4. DRY BREAKING LENGTH ZERO SPAN OF SHEETS FROM THE UNGRAFTED AND VINYL POLYMER GRAFTED CHEMICAL PULP.

1) Bleached softwood kraft pulp (BSKP)
2) BSKP -grafted with acrylamide, loading 63
3) BSKP + BSKP -grafted with acrylamide, loading 63
   Ratio pulp/pulp grafted: 1/1
4) BSKP + BSKP -grafted with acrylamide, loading 63
   Ratio pulp/pulp grafted: 4/1
5) BSKP -grafted with acrylonitrile, loading 72
6) BSKP + BSKP -grafted with acrylonitrile, loading 72
   Ratio pulp/pulp grafted: 1/1
7) BSKP + BSKP -grafted with acrylonitrile, loading 72
   Ratio pulp/pulp grafted: 4/1

S: Sheet not consistent

The dry breaking length, dry zero span breaking length and stretch at break for different ratios of grafted and ungrafted pulp are shown in Figures 3, 4 and 5. Poorer mechanical strength for the papers containing 100% grafted pulp (polyacrylamide, polyacrylonitrile) was observed.

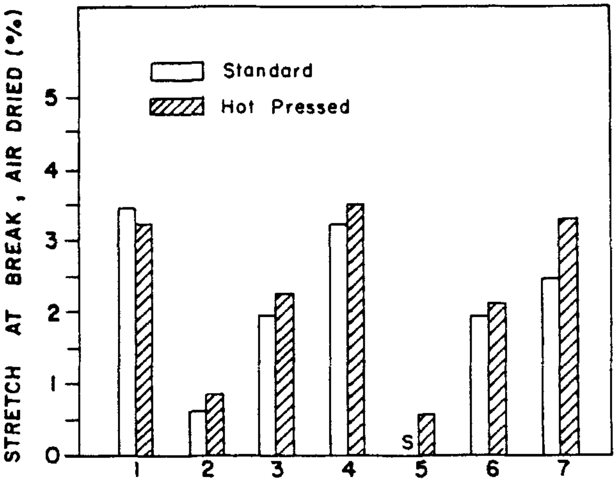


Figure 5. DRY STRECH AT BREAK OF SHEETS FROM THE UNGRAFTED AND VINYL POLYMER GRAFTED CHEMICAL PULP.

1) Bleached softwood kraft pulp (BSKP)
2) BSKP-grafted with acrylamide, loading 63
3) BSKP + BSKP -grafted with acrylamide, loading 63
   Ratio pulp/pulp grafted: 1/1
4) BSKP + BSKP - grafted with acrylamide, loading 63
   Ratio pulp/pulp grafted: 4/1
5) BSKP - grafted with acrylonitrile, loading 72
6) BSKP + BSKP -grafted with acrylonitrile, loading 72
   Ratio pulp/pulp grafted: 1/1
7) BSKP + BSKP -grafted with acrylonitrile, loading 72
   Ratio pulp/pulp grafted: 4/1

S: Sheet not consistent

A general improvement of the sheet properties for paper containing grafted pulp could be obtained by hot pressing (pressing at 50 kg/cm^2 amd heating at 150°C for 60 seconds) as described previously.[18,23] Improvements in the dry mechanical properties for pulp grafted with polyacrylamide were observed. They were better than those of pulps grafted with polyacrylonitrile. For polyacrylonitrile grafted pulps, the presence of hydrophobic nitrile groups decreases the amount of hydrogen bonding and conse-

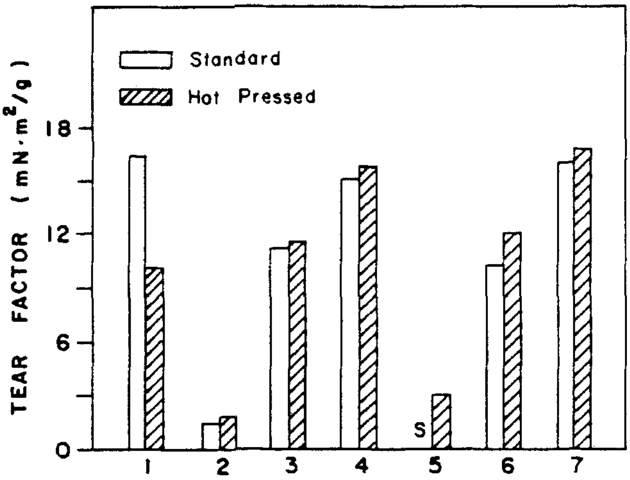


Figure 6. TEAR FACTOR OF SHEETS FROM THE UNGRAFTED AND VINYL POLYMER GRAFTED CHEMICAL PULP.

1) Bleached softwood kraft pulp (BSKP)
2) BSKP -grafted with acrylamide, loading 63
3) BSKP + BSKP -grafted with acrylamide, loading 63
Ratio pulp/pulp grafted: 1/1
4) BSKP + BSKP -grafted with acrylamide, loading 63
Ratio pulp/pulp grafted: 4/1
5) BSKP -grafted with acrylonitrile, loading 72
6) BSKP + BSKP -grafted with acrylonitrile, loading 72
Ratio pulp/pulp grafted: 1/1
7) BSKP + BSKP -grafted with acrylonitrile, loading 72
Ratio pulp/pulp grafted: 4/1

S: Sheet not consistent

quently the resulting paper strength. In the case of acrylamide the decrease in the amount of original OH groups was more than compensated by the increase of amide groups capable of hydrogen bonding.[24] Some improvement of the dry breaking length and dry stretch at break (when compared with the properties of the ungrafted pulp) was achieved with a combination of a small amount of acrylamide grafted pulp and the hot pressing treatment.

These observations are in agreement with our conclusion in a previous paper that the oxidative treatment used to create the active centers on the fiber surface can be detrimental to their mechanical properties.[8]

The same general conclusion can be drawn for the wet sheet properties as shown by the data in the Tables 7 to 9. Hot pressing slightly improved the wet mechanical properties of the paper with grafted pulp. This effect is particularly evident for polyacrylonitrile and is in agreement with previous work.[18,20,24] As shown by Schwab, et al. and Neimo, et al. sheet improvements can be obtained with only a small polymer loading.[25,26] From this study, a small addition of grafted pulp, followed by hot pressing also appears to be a potential way to improve the sheet mechanical properties.

The paper properties can probably be improved further by additional optimization of operating conditions. It is to note that even tear strength could be worth while preserved by appropriate pulp incorporation and treatment (see Fig. 6).

CONCLUSION

THis preliminary work has shown that our grafting process allows the grafting of polyacrylamide or polyacrylonitrile onto cellulosic fibers with excellent grafting efficiencies and polymer loading. Only a modest proportion of grafted pulp in the paper stock is needed to improve the final mechanical properties of the hot pressed paper. In addition, further improvement could be achieved by optimization of the treatment, as well as by minimizing degradation of the pulp in the oxidation steps.

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