were slurried in cold dilute ethanol, filtered, and recrystallized from dilute ethanol to give fine white balls of salicyloyltremuloidin melting at 192–193 °C identified by mixed melting point and identity of infrared absorption spectrum with authentic material (Pearl and Darling, 1965).

The combined filtrates and washings from the salicyloyltremuloidin were spotted on silica gel plates alongside authentic tremuloidin (Pearl and Darling, 1959) and salicyloylsalicin (Pearl and Darling, 1965), developed in the 4:1 chloroform–methanol developer, and sprayed with sulfuric acid to give spots only for these two compounds.

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Scanning Electron Microscopy of Kenaf Paper Structures

Gerald F. Touzinsky, Frederick L. Baker, R. Leo Cunningham, and Marvin O. Bagby*

Scanning electron microscopy was used to study papermaking properties of soda pulps prepared identically from whole kenaf and from its separated bark and core. The behavior of the various cellular materials and fiber preparations was examined at different stages of the web-forming process on a laboratory fourdrinier machine. Critical-point drying was used to preserve the configuration of the mat and the fine structure of the individual fibers. Web structure for all pulps remained very open throughout the wet end, and finally coalesced to form a well-bonded sheet in the last stages of machine drying. Kenaf bark pulp responded to beating much the same as did a southern pine kraft pulp. Core pulp does not become highly fibrillated during beating but shows increased flexibility. On drying, core fibers collapsed into intimate contact to give a tightly compacted sheet. Behavior of whole kenaf pulp was a composite of bark and core behaviors.

Kenaf (*Hibiscus cannabinus*) is a promising, annually renewable, papermaking raw material. Recent economic comparisons of kenaf with pulpwood and major annual crops of the southeastern United States place it in a competitive position (Moore et al., 1976). Pulps with desirable papermaking properties have been prepared by commercial chemical processes (Clark et al., 1962; Clark and Wolff, 1965). Papers containing considerable kenaf fiber in the furnish have been made on commercial paper machines (Clark et al., 1971b; Jeyasingam, 1974; Cathirgamu and Manokeran, 1975).

Being a dicotyledon, kenaf has two distinct regions to its stem: an outer bark and an inner, woody core. Relative to the core, the bark contains more cellulose and correspondingly less pentosan and lignin (Clark et al., 1971a). These chemical differences cause higher yields and greater ease of chemical pulping of the bark (Clark et al., 1971a; Touzinsky et al., 1973). Nieschlag et al. (1961) reported average lengths of 2.60 and 0.60 mm for bark and core fibers, respectively. Core fibers have a lower ratio of cell wall thickness to cell diameter than do bark fibers (Clark et al., 1967), and this contributes to their greater flexibility (Touzinsky et al., 1972). These fiber differences produce the greater strength and porosity of bark sheets and the greater smoothness and density of core sheets (Touzinsky et al., 1972; Nagasawa and Yamamoto, 1970). In combination, bark and core pulps show anomalous strengths exceeding those expected for the combination (Touzinsky et al., 1972). Clark and Wolff (1962) reported related synergistic effects for blends of whole kenaf and wood pulps.

To understand better the strength characteristics and papermaking properties of kenaf, we examined the mechanical behavior of bark, core, and whole kenaf pulps during web formation on a fourdrinier, laboratory paper machine and compared their relative responses to those of a commercial softwood pulp. In this report, we discuss

Northern Regional Research Center, Agricultural Research Service, U.S. Department of Agriculture, Peoria, Illinois 61604.

Table I. Pulping of Kenaf[a]

Pulp	Bark	Core	Whole
Chemical consumed			
Basis appl., %	71.0	75.9	73.9
As Na_2O, %	12.6	13.6	13.3
Yield			
Crude	58.8	48.2	53.1
Screened	58.3	46.4	51.8
Kappa number	9.5	21.0	22.6
Initial freeness			
S.R., mL	855	645	727

[a] Soda cooks 170 °C, 2.0 h, 18.0% active alkali. Values are average of two or three cooks.

our observations made with a scanning electron microscope (SEM) and relate those observations to physical properties of the webs.

EXPERIMENTAL SECTION

Whole kenaf and separated bark and core materials from Maryland-grown green, air-dried kenaf were chopped to approximately 1-in. lengths, cleaned by means of a wet cleaning procedure (Bagby et al., 1972), and pulped by the soda process at 120 °C for 2.0 h using 18.0% applied active alkali in a 0.5 cub ft globe digester. A commercial, southern pine, kraft pulp was included for comparison. Pulps were evaluated in a valley beater. Handsheets and machine sheets were tested according to TAPPI standards.

For the paper machine runs, each pulp was beaten to approximately 500 mL freeness S.R. (Schopper-Riegler) in the Valley beater and formed into a web on a 26 cm wide laboratory paper machine at 1.2 m/min. No sizing or alum was used and no headbox pH adjustment was made. Pulp or web samples were taken for microscopic examination (1) at the headbox, (2) on the wire, (3) after the couch roll, (4) after the press section, (5) after the fourth dryer can, (6) after the last (tenth) dryer, and (7) after the calender stack. Samples were solvent exchanged in three increments (30% ethanol, 70% ethanol, and absolute ethanol). For ease of handling, the first four, more fragile samples were sealed in porous stainless-steel capsules. The others were exchanged to absolute ethanol as webs in jars. All samples were dried by the critical-point drying technique, using metal capsule sample holders as described by Baker and Princen (1975). Mounted samples were coated by vapor deposition with a gold–palladium alloy (60:40) and viewed and photographed in a Cambridge Stereoscan Mark 2A scanning electron microscope (Baker and Princen, 1971). Photographs were taken at 50×, 100×, and 500×.

RESULTS

Pulping and Physical Properties. The bark material cooked more readily than did the core as indicated by the lower alkali consumption and lower Kappa number (Table I). The results for whole kenaf were generally intermediate between bark and core. The strength values for the whole kenaf sheet were also generally intermediate between those of the bark and the core sheets for both the machine-made papers and the handsheets (Tables II and III). However, these experimental values did not approach the weighted arithmetic mean as closely as had been observed earlier in PFI mill runs (Touzinsky et al., 1972). Also, as noted previously (Touzinsky et al., 1972), the values for breaking length were greater for whole kenaf than for either bark or core sheets.

Microscopy. When examined with the SEM, the web prepared from the bark pulp showed very open structure for all samples from the headbox through the press section (Figure 1a). It was only partially compressed in the dryer and was still open after the dryers (Figure 1b). It became

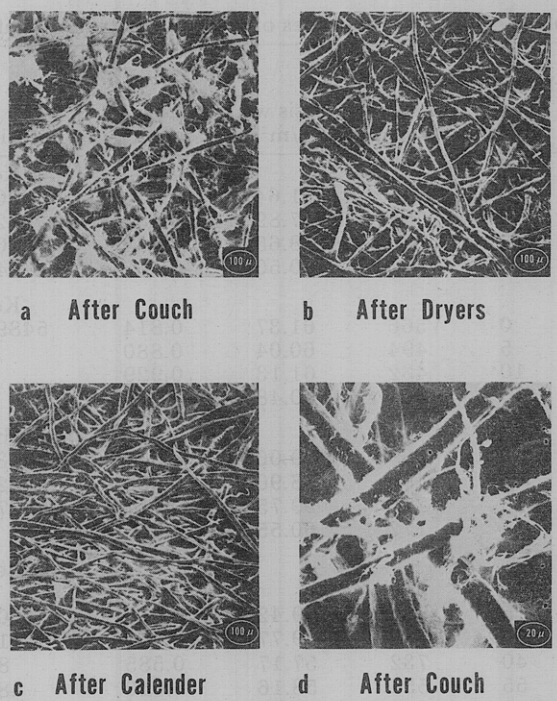


Figure 1. (a) Bark after couch (100×); (b) bark after dryers (100×); (c) bark after calender (100×); (d) bark after couch (500×).

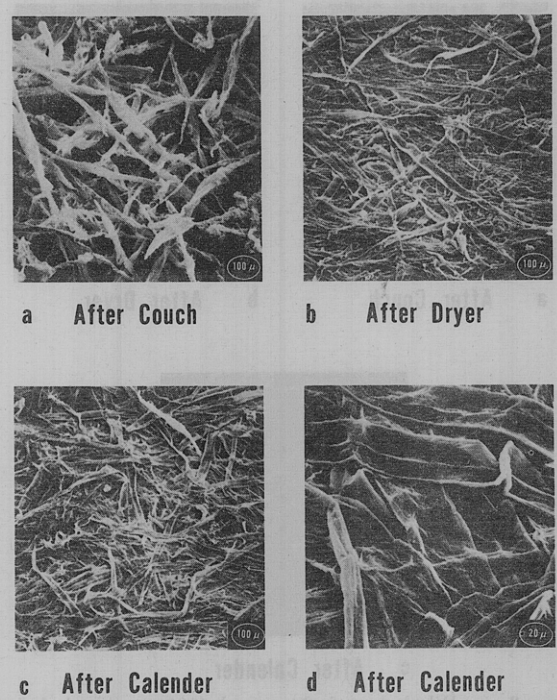


Figure 2. (a) Core after couch (100×); (b) core after dryer (100×); (c) core after calender (100×); (d) core after calender (500×).

fairly tight and compacted during calendering (Figure 1c). Much fine fibrillar material was visible in the samples from the headbox through the couch roll (Figure 1d) and almost as much remained after the press section. Even after the first four dryers, the fibers showed fibrils standing out from the surface. Only after the sheet had passed completely through the dryer section were the fibrils fully collapsed down onto the fibers or into membranous interfiber webs. Similarly, ray-like parenchyma cells, which were distinguishable in the early stages of the papermaking process up through the press section, disappeared in the dryer section, apparently collapsing down onto the fibers and becoming part of the interfiber membranes.

Table II. Physical Properties of Handsheets from Kenaf Pulps

Refining time, min	Freeness S.R., mL	Basis wt, g/m²	Density, g/cm³	Porosity, s	Burst factor, (g/cm²)/(g/m²)	Tear factor, g/(g/m²)	Breaking length, m	MIT fold	Strength[a] index
				Kenaf Bark Pulp					
0	812	61.64	0.435	0.8	28.5	271.0	5385	75	2435
5	708	57.89	0.480	2.8	44.1	217.2	8336	326	2885
15	536	58.65	0.533	20.5	56.7	168.0	9980	614	2985
25	366	60.50	0.563	64.4	57.6	159.7	9144	623	2950
				Kenaf Core Pulp					
0	566	61.37	0.814	5489.9	37.3	44.8	7082	225	1590
5	494	60.04	0.880		51.7	40.0	9725	399	1750
10	432	61.13	0.929		59.4	37.7	8986	1060	1890
15	374	60.48	0.939		63.5	33.9	9413	1441	1895
				Whole Kenaf Pulp					
0	566	59.06	0.599	343.2	43.2	108.9	9413	251	2245
5	498	58.90	0.639	882.0	52.1	99.4	10705	394	2380
15	276	59.75	0.711	3407.9	54.1	79.8	10465	405	2240
25	172	60.55	0.756		57.9	69.2	10040	494	2210
				Southern Pine Kraft Pulp					
0	918								
15	888	59.42	0.518	0.7	31.1	229.4	5766	174	2520
25	862	59.77	0.550	1.5	41.7	182.0	6624	422	2710
40	732	57.17	0.585	8.2	48.6	150.0	7812	484	2695
55	554	58.16	0.610	48.9	56.1	134.2	8367	764	2790
70	352	59.91	0.636	256.1	57.2	129.9	9035	803	2785

[a] Modified Haywood procedure (Cunningham et al., 1970).

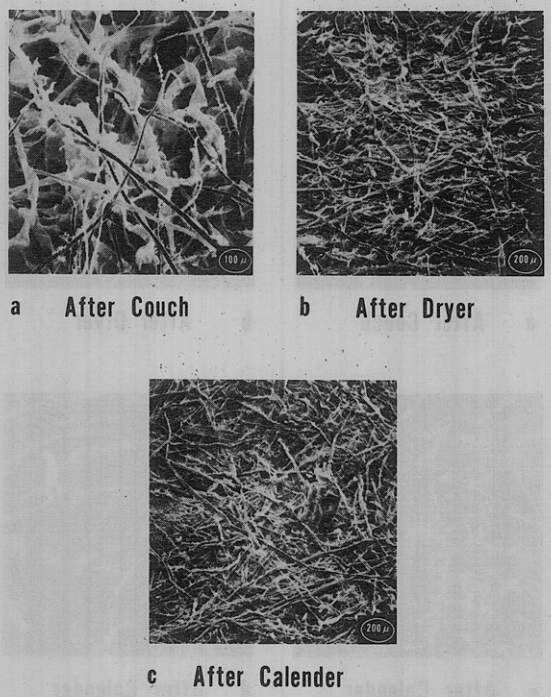


Figure 3. (a) Whole kenaf after couch (100×); (b) whole kenaf after dryer (50×); (c) whole kenaf after calender (50×).

Webs from core pulps were completely open structures at all stages of papermaking up through the press section (Figure 2a). Some fibrils remained extended through the press section but coalesced while drying. Fibrillation was confined to the fibers and did not occur on the ray- or vessel-like cells. After the dryers, the sheet structure, as a whole, and the fiber elements within it were completely collapsed (Figure 2b). All fibers were flat ribbons dried down onto and conforming to the surface of the elements beneath (Figure 2d). Calendering produced essentially no visible effect at the magnifications used (Figure 2c).

The web from the whole kenaf pulp was very open through the press section (Figure 3a), more so than that

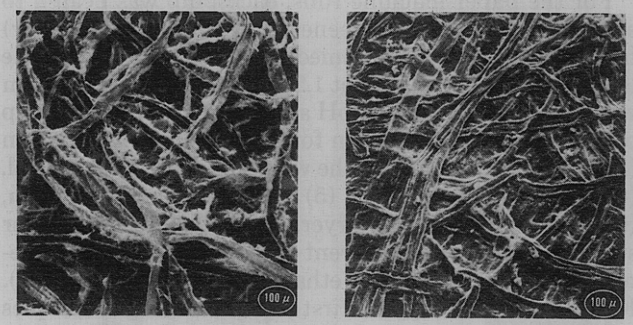


Figure 4. (a) Southern pine after press (100×); (b) southern pine after dryer (100×).

of the bark pulp, and almost as open as that of the core pulp. In the dryer, the structure flattened and the majority of the thin-walled cells collapsed (Figure 3b). Further flattening of the paper web structure, observable only at the lowest (50×) magnification, occurred after the calender (Figure 3c). The effect was much less apparent than with the bark pulp. Suspended fibrils were present through the press section on the bark fibers but not to the extent observed in the papers prepared from all bark fiber. After drying, the structure was quite closed up, but not as tightly as that of the web from all core pulp.

The southern pine pulp webs were open through the press section but formed a relatively closed structure after partial drying (after the first four dryers). Fibrils remained uncollapsed through the press section (Figure 4a), but were much less prominent in the sample taken in the dryer section. After drying, all fibrils had compressed onto the fibers and into the interfiber spaces. Essentially, all thin-walled, earlywood fibers had collapsed (Figure 4b). Calendering compacted the web further.

The mechanical response of the sheet structures to calendering differs somewhat from their response as seen in the SEM. While the bark sheet showed the most visible change, the density of the whole kenaf sheet increased most (14.4%). Even the core sheet, which changed the

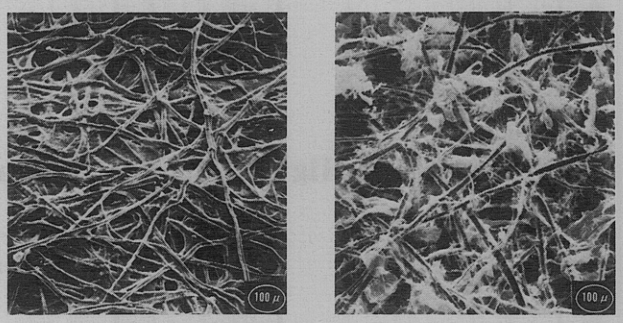
Table III. Physical Properties of Machine-Run Papers

Beating time, min	Freeness S.R., mL	Calendering[a]		Basis wt, g/m²	Density, g/cm³	Porosity, s	Burst factor, (g/cm²)/(g/m²)	Tear factor, g/(g/m²)	Breaking length, m	MIT fold
					Kenaf Bark					
17	489	Unc	MD	53.0	0.423	5.5	25.8	196	6687	251
			CD					189	4777	268
		Cal	MD	54.5	0.469	6.7	19.4	182	6260	271
			CD					166	4475	137
					Kenaf Core					
5	509	Unc	MD	45.1	0.601	1684.1	39.6	42	9734	484
			CD					46	6628	148
		Cal	MD	45.5	0.642	1499.5	38.8	54	9227	318
			CD					49	5682	275
					Whole Kenaf					
5	519	Unc	MD	59.9	0.493	130.4	37.8	103	10422	269
			CD					115	5701	105
		Cal	MD	57.0	0.564	171.7	34.8	90	10735	355
			CD					107	5544	103
					Southern Pine Kraft					
69	550	Unc	MD	58.7	0.505	14.9	24.2	149	7089	668
			CD					160	3704	222
		Cal	MD	49.7	0.575	11.3	21.8	129	6304	534
			CD					114	3569	190

[a] MD, machine direction; CD, cross direction; Unc, uncalendered; Cal, calendered.

least, showed a fairly large change (6.8%).

The critical-point drying procedure used to prepare the samples for SEM preserves the overall web structure as well as fine fiber structure, as mentioned by Parham (1975). Samples of the very wet bark pulp web were taken after the couch, after the press, and in the dryer and were dried in air rather than by the critical-point drying method. These samples retained none of the open structure and extended fibrils seen in the corresponding critical-point dried samples, but appeared almost identical with the critical-point dried samples taken after the dryer (Figure 5a and 5b).



a After Couch, Air Dried b After Couch, C.P. Dried

Figure 5. (a) Air-dried kenaf bark after couch (100×); (b) bark after couch, critical-point dried (100×).

DISCUSSION

There were two major differences observed between the bark and the core pulp. The first was their response to beating. Bark pulp fibers peeled and fibrillated in much the same way as southern pine pulp. The result was considerable fine material which collapsed into interconnecting structures when the web was dried. Core pulp fibers showed very little surface response to beating. What little fibrillation occurred took place only on the thick-walled, true fibers. A small amount of fines was generated by disintegration of thin-walled parenchyma cells. The main response to beating seemed to be an increase in core fiber flexibility.

The second major difference between bark and core pulps lay in their web formation and coincident response to drying. Both fiber types produced open structures and essentially random distributions. The core fibers, being smaller and more flexible than the bark fibers, showed more bends and twists and gave the appearance of forming a more tortuous mat. When dried, the bark fibers generally retained their original shape and formed open spaces or gaps between fibers, which were bridged by other fibers. The core fibers, however, flattened down on one another, conforming to the surfaces of the fibers below them and completely closing up the web. These differences are related predominantly to fiber morphology rather than chemical composition or response to pulping.

The behavior of bark fibers in papermaking is essentially that of long, fairly flexible fibers, both in their formation or arrangement in the sheet and in their contribution to the strength properties of the sheet. Bark fibers and papers resemble those of commercial pine kraft closely, except in their more rapid rate of beating.

The core fibers, even at their significantly higher lignin content (Kappa no. of 21 vs. 10 for the bark), are much more compliant. In the sheets, they pull the entire web together and cement it into an almost homogeneous mass.

The whole kenaf sheet is a composite of the individual properties of the two types of fibers. The bark fibers show some fibrillation; the core fibers do not. Both fibers, of course, give an open structured wet web. During drying, the results of their interaction becomes apparent. In the early stages, the effects of the core pulp predominate by contracting the structure and bonding the fibers. Later, the longer, stiffer bark fibers resist this compaction and prevent it from becoming as complete as in the core webs. The bark fibers contribute strength properties related to fiber length, such as the greater tear strength, and a greater apparent response to calendering. The core fibers contribute increased bonding and sheet density.

SUMMARY

Scanning electron microscopy after critical-point drying has shown us that both the bark and the core fibers contribute strongly to the properties of the whole kenaf sheet. These fibers interact as do the blends of commercial

pulps that comprise most paper furnishes and give us an array of properties beyond those available from each type individually.

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Modification of High-Yield Pulp Fibers by the Xanthate Method

Raymond A. Young

A series of high lignin content pulps has been graft copolymerized with acrylonitrile, styrene, and acrylamide by the xanthate method. The degree of conversion of monomer to polymer and percent grafted polymer were much lower for modification reactions with mechanical pulps (stone groundwood, thermomechanical) than with chemical (kraft, oxygen) and semichemical (neutral sulfite semichemical) pulps. The amount of grafted polymer appears to be correlated with the lignin content of the pulp. Enhanced levels of grafting for high-yield kraft and thermomechanical pulps can be realized when binary mixtures of monomers are used in the reaction media. Differences in reactivity and surface properties of the pulp fibers are discussed in relation to the modification reactions.

Methods for chemical modification of pulp fibers are being investigated as part of a continuing research program on the structure and bonding of flexible fiber composites at the University of Wisconsin. Such composites include both synthetic papers and nonwoven fabrics and represent a fiber end-use of increasing importance. The further penetration of pulp products into nonwoven markets will be substantially influenced by fiber characteristics and bonding considerations and in turn will be appreciably affected by the chemical composition of the fiber. It would be highly desirable if the modification reactions were applicable to pulp fibers of high lignin contents. This not only would increase potential yields and lower costs, but would also avoid some of the pollution problems associated with waste lignins from pulping and bleaching.

One widely studied technique of fiber modification is the grafting of vinyl monomers to cellulosic fibers (Phillips et al., 1972; Stannett, 1970; Stannett and Hopfenberg, 1970). However, the overwhelming majority of research has been on grafting rather pure forms of cellulose and, indeed, most grafting reactions are not amenable to lignin-containing cellulose fibers. Recently, however, several investigators have reported methods for modification of high-yield fibers (Rånby and Hatakeyama, 1975; Hornof et al., 1975a, 1976). Hornof et al. (1975a,b) have utilized a technique involving xanthation of the cellulose fiber prior to the formation of the free radicals. The method takes advantage of the capability of cellulose xanthates to form a redox couple with a suitable agent. The essential re-

Department of Forestry, School of Natural Resources, College of Agriculture and Life Sciences, University of Wisconsin, Madison, Wisconsin 53706.