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Wood Chemical Composition as Related to Properties of Handsheets Made from Loblolly Pine Refiner Groundwood

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Summary

Burst and tear strengths of handsheets made from 48 pulps disk-refined from chips of varying chemical composition decreased with increasing extractive content after the independent effects of fiber morphology were specified. This result was attributed to lessened bond strength caused by reduced surface tension forces and blocking of reactive sites on the fiber surfaces.

Zusammenfassung

Berstzahl und Reißfestigkeit der Blätter von 48 verschiedenen Zellstoffen aus scheibengemahlenen Spänen mit unterschiedlichen chemischen Bestandteilen verringerten sich mit ansteigendem Extraktstoffgehalt; die davon unabhängigen Einflüsse des Faseraufbaues sind dabei berücksichtigt. Diese Tatsache wird der verminderten Bindungskraft zugeschrieben, verursacht durch die herabgesetzte Oberflächenspannung und die Blockierung von Bindungsstellen an den Faseroberflächen.

Introduction

Two previous papers [MCMILLIN 1968b, 1969] have examined gross wood characteristics, fiber morphology, and degree of refining in relation to sheet properties as part of a program to develop criteria useful in predicting and controlling the papermaking potential of loblolly pine (*Pinus taeda* L.) refiner groundwood.

These studies revealed that most sheet properties could be improved and made more uniform by isolation or selection of wood having the desired gross characteristics of high latewood content but relatively low density. It was further shown that fiber prepared from wood having long, narrow-diameter tracheids with thick walls yielded handsheets of improved properties. This was attributed to the ability of such tracheids to unwind into highly deformable, ribbon-like particles as a result of torsional stresses induced during the final phases of refining. Research elsewhere [FORGACS 1963] has shown such ribbon-like particles to provide the coherence necessary for strength development in mechanical pulps.

The present study was undertaken to determine whether wood chemical composition affects sheet properties after the effects of wood morphology have been considered. A subsequent paper will examine pulp quality in relation to handsheet strength.

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Procedure

The detailed procedures for selection of trees, wood preparation and classification, refining, chip sampling, and handsheet testing have all been described previously [McMillin 1968b]. All chemical constituents were determined from sample chips used in the earlier studies and were correlated with the previously measured sheet properties.

While pulps for the series of studies were produced by both single- and double-pass refining, this paper deals only with those from double-pass fiber. Specific refining energy was 40 hp days per air-dry ton on the first pass and 30 hp days per air-dry ton on the second.

Wood was selected and stratified into 12 categories. Two growth rates, two specific gravities, and three radial positions in the tree were considered in a factorial design. The wood in each category was chipped and the chips randomly divided into four within-sample replications. Before refining, a subsample of 1000 chips was drawn from each replication for evaluation of wood properties.

Five chemical constituents were measured: hemicellulose, holocellulose, alpha-cellulose, lignin, and extractives. They were correlated with four sheet properties: sheet density, burst factor, tear factor, and breaking length.

Chemical constituents were determined from 100 chips randomly selected from each subsample. The chips were air-dried and ground to meal in a Wiley mill. The fraction passing a 40-mesh screen and retained on a 60-mesh screen was then conditioned to equilibrium moisture content in a room maintained at a constant 50 percent relative humidity and 72° F.

Holocellulose and alpha-cellulose were determined by the method of Erickson [1962], except that the amount of sodium chlorite solution per cycle was doubled for the holocellulose determinations. Hemicellulose values were calculated as the difference between holocellulose and alpha-cellulose values. Duplicate determinations were made for each of the 48 samples, and the averaged result was expressed as a percentage of the weight of ovendry extractive-free wood.

The alcohol-benzene extractive content was determined in accordance with TAPPI standard method T 6 os-59 and expressed in percent of ovendry weight. Lignin content, expressed as a percentage of ovendry extractive-free wood, was determined by the TAPPI method given in T 13 m-14.

Table 1 lists the results of the chemical determinations. The handsheet properties are those obtained in the earlier study [McMillin 1968b]. These data, along with the previously determined weighted average for latewood-earlywood morphological characteristics [McMillin 1969], were employed in multiple regression analysis. The analysis followed a sequence of first considering the effect of fiber morphology [McMillin 1969] and then introducing chemical factors by the usual stepwise regression criteria. All equations are of the type $y = b_0 + b_1 x_1 + b_2 x_2 + \cdots$ where y is a dependent variable, e.g., burst, tear; b_i, a regression coefficient; and x_i, an independent variable, e.g., a morphological characteristic or a chemical constituent. Thus, the equations reveal the significant effects on sheet properties of wood chemical constituents after the effects of fiber morphology have been considered. Various transformations of the chemical data were considered, e.g., the square of extractive content and the ratio of alpha-cellulose content to extractive content. The equations were tested at the 95 percent level of probability, and all variables included were significant at that level.

Results

The 48 samples represented in Table 1 exhibited a range of chemical properties. Holocellulose ranged from 68.44 to 75.63 percent; alpha-cellulose, from 43.90 to 53.24 percent; hemicellulose, from 17.59 to 28.81 percent; lignin, from 27.11 to 33.16 percent; and extractives, from 2.49 to 14.20 percent.

Table 1. *Results of Chemical and Handsheet Determinations*[1]

Position in tree (rings from pith)	Unextracted specific gravity	Rings per inch	Holocellulose %	Alpha-cellulose %	Hemicellulose %	Lignin %	Extractives %	Sheet density g/cm³	Burst factor	Tear factor	Breaking length
0 ... 10	0.427	4.11	70.81	44.82	26.00	29.24	6.31	0.289	3.34	41.7	604.3
0 ... 10	.457	7.59	72.53	45.82	25.45	28.99	7.74	.281	3.25	42.2	720.5
0 ... 10	.492	4.80	71.84	46.25	25.59	29.32	10.42	.266	3.82	48.9	761.0
0 ... 10	.515	11.83	70.76	45.96	24.72	30.26	12.84	.293	2.96	35.5	656.1
11 ... 20	.445	5.53	70.34	45.60	24.74	28.99	5.75	.287	4.41	54.3	896.1
11 ... 20	.459	7.08	71.43	47.23	24.33	28.81	4.07	.293	4.87	58.4	996.1
11 ... 20	.512	5.30	73.19	49.86	23.35	28.76	4.12	.318	6.42	82.2	1,264.0
11 ... 20	.524	12.38	71.46	48.20	23.14	29.14	5.73	.292	3.23	41.3	724.2
21 ... 30	.458	4.91	70.40	47.32	23.08	30.21	3.38	.291	5.61	67.0	1,096.9
21 ... 30	.438	8.27	71.28	46.09	25.20	29.84	3.27	.319	7.00	76.5	1,312.4
21 ... 30	.534	5.53	69.78	46.48	23.30	30.45	2.91	.302	5.49	61.3	1,085.3
21 ... 30	.511	8.27	73.37	50.37	23.00	27.42	3.19	.299	5.67	61.7	1,129.3

Table 2 lists multiple regression equations which most accurately describe handsheet properties in terms of weighted average morphological characteristics and chemical constituents. The cumulative R^2 values and the standard errors of the estimates are also given.

When the effects of fiber morphology had been accounted for (Eq. 1), no chemical component was significantly related to sheet density. The effects of fiber morphology on sheet density as well as on the other handsheet properties considered here have been discussed previously [MCMILLIN 1969].

After effects of fiber morphology had been considered, the ratio of alpha-cellulose content to extractive content proved significantly related to burst factor (Eq. 2). These two chemical constituents accounted for an additional 10 percent of the variation in burst beyond the 48 percent accounted for by morphological characteristics.

Figure 1 charts the effect on burst factor of extractives at two alpha-cellulose contents. The graphed lines in this figure and in Fig. 2 were obtained by substituting a range of values for the chemical constituent on the X-axis and fixing the remaining chemical variables in the regression equations at the indicated levels. In all cases, mean values were used for the morphological functions.

[1] Each numerical value is the average of four replications except that values for rings per inch are based on one observation apiece.

Table 2. *Multiple Regression Equations Developed to Describe Sheet Properties in Terms of Wood Morphology and Chemical Constituents*[1]

Property	Equation number	Variable	Coefficient		Cumulative R^2	Standard error of estimate
Sheet density	1		b_0	0.2451		
		$\frac{(TL)(CWT)}{(TD)}$	b_1	0.7350	0.169	0.02
Burst factor	2		b_0	0.8558		
		$\frac{(TL)(CWT)}{(TD)}$	b_1	5.5827	0.373	
		$\frac{2(CWT)}{(LD)}$	b_2	−2.2541	0.477	
		$\frac{(AC)}{(EC)}$	b_3	0.1617	0.584	0.93
Tear factor	3		b_0	714.4824		
		$\frac{2(CWT)}{(LD)}$	b_1	−219.3612	0.378	
		$\frac{(LD)}{(TD)}$	b_2	−988.1338	0.434	
		$\frac{(TD)}{(TD-LD)}$	b_3	26.8053	0.518	
		$(CWT)^2$	b_4	0.7299	0.563	
		$(EC)^2$	b_5	−0.0882	0.602	9.81
Breaking length	4		b_0	13,285.3726		
		$\frac{(TL)(CWT)}{(TD)}$	b_1	3,660.5067	0.453	
		$\frac{2(CWT)}{(LD)}$	b_2	−4,602.1215	0.556	
		$\frac{(LD)}{(TD)}$	b_3	−18,318.4190	0.597	
		$\frac{(TD)}{(TD-LD)}$	b_4	537.5837	0.691	
		$\frac{(TL)}{(TD)}$	b_5	−19,569.7859	0.740	133.20

[1] TL = weighted average tracheid length (mm); CWT = weighted average cell wall thickness (μm); LD = weighted average lumen diameter (μm); TD = weighted average tracheid diameter (μm); EC = alcohol-benzene extractive content (percent); AC = alpha-cellulose content (percent).

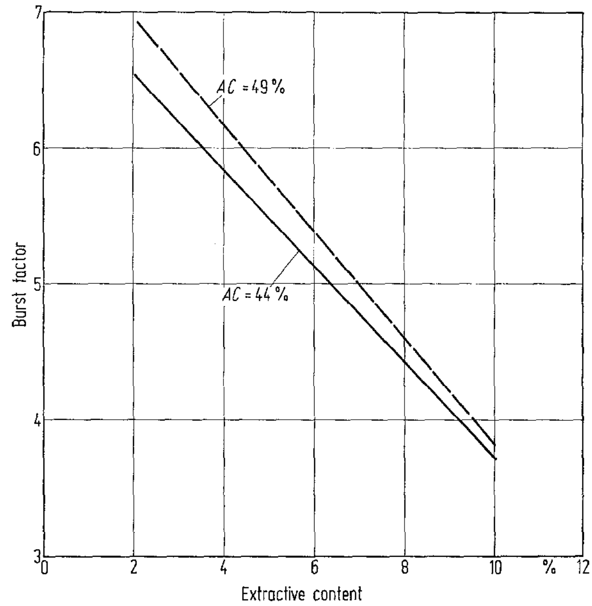

Fig. 1. Burst factor as related to alpha-cellulose content (AC) and extractive content.

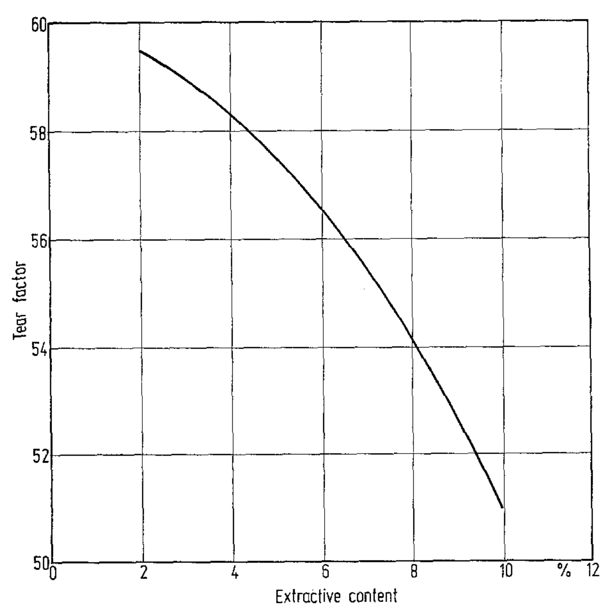

Fig. 2. Tear factor as related to extractive content.

The relations plotted consider only the range of variation in extractive content contained within the range of alpha-cellulose contents and mean values of the morphological variables in question.

Burst decreased with increasing alcohol-benzene extractive content for wood of both high (49%) and low (44%) alpha-cellulose content. For a given extractive content, burst increased with increasing alpha-cellulose content, although the effect of this variable on burst was slight.

The square of extractive content proved a significant chemical variable affecting tear factor after the effects of wood morphology had been considered (Eq. 3). Extractive content accounted for an additional 4 percent of the total variation in tear beyond the 56 percent explained by morphological characteristics.

Figure 2 shows the effect of extractive content on tear factor at mean morphological characteristics. Tear factor decreased with increasing extractives; the rate increased with increasing extractive content.

No chemical constituent proved significantly related to breaking length after the effects of fiber morphology had been accounted for (Eq. 4).

Discussion

As previously noted, no chemical constituent exhibited a significant effect on sheet density after weighted average morphological characteristics had been considered. This outcome seems reasonable, since sheet density is a measure of the solid fraction of the sheet and is essentially governed by the flexibility and wet plasticity of the pulp fibers. When long, thick-walled tracheids of narrow diameter are specified in Eq. (1), the morphological characteristics conducive to ribbon formation have been established [McMillin 1969]. The presence of a high proportion of such ribbons gives rise to a considerable degree of conformability within the sheet, thus producing a sheet of high density.

Although no chemical constituent exhibited a significant effect on breaking length, it should be noted that 74 percent of the total variation in this property was accounted for by specifying fiber morphology. Hence, from a statistical point of view, a relatively small percentage of the total variation in breaking length remained unaccounted for. Extractives probably affect breaking length, but in this test the variation could not be detected after the effects of fiber morphology had been considered.

It is not unreasonable to expect extractives present in the pulp to have a detrimental effect on handsheet strength, especially on those properties dependent upon the number and quality of fiber-to-fiber hydrogen bonds established in the paper mat.

It is generally held that water aids in bringing the cellulosic fibers into sufficiently close contact for hydrogen bonding. As water is removed from the fibrous mat, small fillets or menisci of water between fibers replace the continuous water. The surface-tension forces developed within these menisci have components tending to bring the fiber surfaces into intimate contact.

A pure cellulosic surface is hydrophilic and easily wettable; that is, it exhibits a low contact angle with water. Thus, surface-tension forces are high. Extractives tend to contaminate the surface of fibers. A hydrophobic condition is created, wettability is reduced, and a high contact angle is formed between the fiber and the water. Surface-tension forces are proportionately lowered, reactive sites on the fiber surface are blocked, and the number of effective hydrogen bonds is reduced. Sheets of inferior strength result.

The extractives themselves may also undergo chemical reactions that reduce sheet strength. For example, oxidation will increase the acidity of the fiber mat, promoting fiber degradation and weakening the bonds.

It was further observed that the color of the pulps and the color of handsheets made from the pulps were considerably influenced by the amount of extractives. Pulps of high extractive content were dark and produced dark sheets. This is reasonable since high proportions of extractives are retained in refiner groundwood pulp.

The detrimental effects of extractives on sheet properties reported here are in general agreement with those found by BRANDAL and LINDHEIM [1966] for groundwood pulps of Scotch pine and Norway spruce. It is of significance that fibers of dimensions needed for coherence and strength development (long tracheids with thick walls and narrow diameters) are most abundant in mature wood [McMILLIN 1969]. In a previous study [McMILLIN 1968a], extractive content of loblolly pine wood was shown to be independently related to rings from the pith and specific gravity but unrelated to growth rate. Extractive content decreased with increasing rings from the pith; for a given ring it increased with increasing specific gravity, but the difference in extractives between wood of high and low density was minor in the mature outer wood (25 rings from the pith). Thus, if mature wood is specified, extractive content will necessarily be low as a result of the independent negative effect of rings from the pith. Furthermore, the range in variation of extractives due to the independent effect of specific gravity will be small. It may be concluded that the negative effect of extractives on handsheet strength is of secondary importance when the wood selected for pulping has the desired cellular morphology.

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