Comparison of Physical, Chemical, and Thermal Characteristics of Water-, Dew-, and Enzyme-Retted Flax Fibers

H. S. S. SHARMA,^{1,2} G. FAUGHEY,¹ G. LYONS^{1,2}

¹ Department of Applied Plant Science, School of Agriculture and Food Science, The Queen's University of Belfast, Newforge Lane, Belfast BT9 5PX, United Kingdom

² Applied Plant Science Division, Department of Agriculture for Northern Ireland, Newforge Lane, Belfast BT9 5PX, United Kingdom

Received 12 November 1998; accepted 13 February 1999

ABSTRACT: Assessments of dew-, water-, and enzyme-retted fibers for differences in fineness, strength, caustic weight loss, acid detergent fiber, neutral detergent fiber cellulose, hemicellulose, lignin, carbon, hydrogen, nitrogen, lipid, ash, and nine minerals were compared in this study. Distinct differences in retted-fiber samples were observed in all the parameters tested. The samples also were analyzed by derivative thermogravimetry, which revealed that weight losses in two decomposition bands of $240-400^{\circ}$ C and $400-520^{\circ}$ C correlated with the fiber fineness and the caustic weight-loss measurements of the samples. The variations in quality of the fiber samples were mainly due to differences in the proportion of residual noncellulosic polysaccharides, lipid, lignin, and certain minerals. The key parameters for determining fiber quality are fiber fineness, strength, ash, caustic weight loss, and the derivative thermogravimetry weight-loss parameters. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 139–143, 1999

Key words: flax; dew-, water-, and enzyme-retted fiber; physical, chemical, and thermal quality characteristics

INTRODUCTION

Cellulose is the major constituent of flax fiber and the minor constituents are noncellulosic polysaccharides, such as pectin and hemicelluloses, lignin, lipids, and ash.^{1,2} Although most of the noncellulosic components present in the fiber are removed during retting and scutching (mechanical separation of the fiber), poor quality fiber can contain as much as 20-25% of the hemicelluloses, pectin, and lignin.^{3,4} Airflow, tensiometer, and caustic weight-loss methods, respectively, are routinely used to determine fiber quality, fineness, tensile strength, and degree of retting. In addition, other tests including fluidity, moisture regain, and fiber distribution also are determined for detailed assessment of fiber quality. However, the traditional methods for fiber assessment are long winded and labor intensive and, as a result, rapid instrumental measurement of fiber quality has long been an area of interest.⁵

Earlier reports^{6–8} on the application of thermogravimetry (TG) were on the assessment of cotton and wood fibers. The use of TG to determine differences in thermal stability of flax fibers at different heating rates and also changes that occur in the thermal spectrum during sequential chemical processing of linen fabric samples, was first reported by Sharma and Kernaghan.⁵ Studies on the thermal properties of cellulose have

Correspondence to: H. S. S. Sharma.

Journal of Applied Polymer Science, Vol. 74, 139-143 (1999)

^{© 1999} John Wiley & Sons, Inc. CCC 0021-8995/99/010139-05

produced conflicting data as results obtained are difficult to correlate due to differences that exist between various types of fibers, such as crystallinity, degree of polymerization, carboxyl, and carbonyl contents.⁶⁻⁸

Comparisons of physical properties of waterand dew-retted fibers have been investigated by various researchers;^{9,10} however, detailed assessments of physical, chemical, and thermal characteristics of fibers obtained from different retting treatments have not been reported. The goals of the present investigation were to establish relationships between physical, chemical, and thermal characteristics of water-, enzyme-, and dewretted fibers and to provide key parameters for assessing fiber quality.

MATERIALS AND METHODS

Flax Sample

The fibers used in this investigation were of the following types: dew-retted (three commercial samples, Villenuve, France), water-retted (three commercial samples, Ghent, Belgium), enzymeretted fiber (three experimental samples obtained from trials performed in Northern Ireland using Flaxzyme (Novo Industry, Copenhagen, Denmark), and fiber scutched from unretted straw (three samples, Belfast, Northern Ireland). Protocols for growing, production of straw and extraction of unretted fiber and enzyme-retting have been described previously.^{10,11} The unretted fiber samples were included in this investigation to provide a general guideline of fiber composition before removal of noncellulose polysaccharides during retting.

Physical Assessment

The samples were also assessed for handle, luster, and color. Fiber fineness was determined on 2.5-g samples by the air-flow method of the British Standards Institute (BSI) using a Wool Industries Research Association fineness meter (Reynolds & Brandson Ltd, Leeds, UK). The tensile strength of the fiber was calculated as the mean of 50 individual fibers of 1-cm test length measured according to the recommended methods of the BSI using a Tensiometer (Instron, High Wycombe, UK).¹²

Chemical Analyses

All samples were air dried at room temperature and then milled to pass through a 0.5-mm mesh

size. The proportion of noncellulosic fractions including pectin present in the fiber was determined using the caustic weight-loss method by treating oven-dried cut fiber (3 g) with 2 M NaOH solution (100 ml) for 4 h. After redrying to constant weight, the loss (%) in weight was calculated from a mean of three replicates.¹³ Low weight loss signified better-quality fiber.

The major fiber components, such as cellulose, hemicellulose, and lignin of the samples were determined by acid detergent and neutral detergent methods¹⁴ as the acid detergent fiber (ADF) and the neutral detergent fiber (NDF). The ADF fraction contains cellulose and lignin, and the NDF fraction contains cellulose, hemicellulose, and lignin. The lignin fraction was determined by the sulfuric acid method followed by refluxing in ADF solution.¹⁵ Cellulose and hemicellulose fractions were the difference of ADF-lignin and NDF-ADF, respectively. The ash, mineral, and lipid contents were determined by methods recommended by the Society of Analytical Chemists.¹⁶ Each sample was analyzed in triplicate.

Elemental Analysis

The cut fiber samples retained in aluminum vials were analyzed by elemental analysis. This was achieved by combusting the samples (6-7 mg) in pure oxygen with an inert carrier gas (argon). The resultant gases such as carbon dioxide, water, and nitrogen dioxide were measured as carbon (C), hydrogen (H), and nitrogen (N), respectively, using gas chromatography (PE 2400 CHN). Each sample was analyzed in triplicate.

Thermogravimetric Analysis

The fiber samples for TG analysis were subsampled from middle, root, and top ends of the fiber length to reduce variation during the comparative assessments. The samples were cut into 2-mm lengths and TG analysis of the cut fiber (3–3.2 mg) was determined in a microbalance (Mettler, MT 5) suspended in a furnace (TG 50). This was controlled by a processor connected to a computer for calculating the first derivative from the weight-loss data using STAR software (Mettler Toledo, Leicester, UK). The TG system was flushed with air (20 mL/min) at 25 to 600°C at a rate of 20°C rise/min. Each sample was tested in triplicate.¹⁷

Reference samples were also analyzed by DTG to aid in the identification of the structural com-

ponents present in the fiber. The samples with their manufacturer and product code are listed: cellulose (Sigma, C-8002, Dorset, UK), araban (Koch-light, 0444-00, Suffolk, UK), D (+) xylose (Sigma, X-1500), Na-polypectate (Sigma, P-1879), amylopectin (Sigma, A-8515), cellulose (Sigma, C-4888), levoglucosan (Sigma, A-8417), and lignosulphonic acid (Aldrich, 37097-5). The results of the physical, chemical, and thermal analyses of the fiber samples were analyzed statistically by ANOVA and correlations between some of the important parameters were calculated to highlight the relationships.

RESULTS

Physical and Chemical Analyses

Comparison of the retted samples for handle and luster showed that water-retted fibers were the best and unretted fibers were the poorest. The color of the fiber ranged from green in unretted materials to pale yellow in water-ret samples. The comparison of fiber fineness, strength, and caustic weight loss of the test fibers has shown that increase in fiber fineness correlated with lower caustic weight loss (r = 0.876). The proportions of hemicelluloses present in unretted fiber were lower than in dew-, water-, or enzyme-retted fiber samples. The water-retted samples were stronger compared with the other samples, although the differences were not significant (Table I). The proportions of ADF, NDF, cellulose, and lignin fractions present in the retted and unretted fiber samples were significantly different (p < 0.05). Of the three retted types of fiber, proportions of ADF, NDF, and cellulose fractions were highest in enzyme-retted samples (Table I). Comparisons of C, H, N, ash, and lipid contents of the samples have shown that carbon and lipid contents were proportionally lower in unretted fibers compared with the retted fiber and maximum ash was detected in unretted and dew-retted fiber. Hydrogen and nitrogen levels were highest in dew-retted fiber, but the differences were not significant (Table I).

The fiber fineness measurements correlated positively with Mg (0.909) and K (0.844), and negatively with NDF (-0.817). The NDF fractions correlated negatively with Na (-0.760) and lipid (-0.942). The variations in the concentrations of P, Mn, Mg, Na, K, and Zn present in all the fiber types were significant (Table I). Unret-

ted and dew-retted fibers contained higher levels of P, Mn, Mg, K, and Zn. High concentration of Ca was detected in all four types of fiber. However, the differences in Ca concentrations were not significant (Table I).

Thermal Analyses

The major weight losses of the primary peak (WL-PP) ranging from 55-64%, representing pectin, hemicellulose, and cellulose, ⁵ occurred in the temperature band of 240-400°C (Table I). Peak pyrolysis temperatures of retted fiber were near 355°C in contrast to 341°C for unretted fiber. In the decomposition range of 400-520°C, a weight loss (WL-SP) representing the residual thermal stable components including lignin⁵ was detected and this ranged from 27 to 32%. High weight loss in the primary peak was associated with low weight loss in the secondary peak. The decomposition temperatures of unretted and enzyme-retted fiber were lower compared with the same for water- and dew-retted samples (Table I).

The weight loss in the primary peak of the thermograms was correlated positively with ADF (0.801), NDF (0.861), and cellulose (0.758), and negatively with caustic weight loss (-0.709), P (-0.897), Mn (-0.883), and K (-0.889). In contrast, the same in the secondary peak correlated positively with P (0.765), Mn (0.839), and K (0.833). The relationship between DTG parameters and fiber fineness was examined to identify the possibility of measuring fineness from the weight-loss data. The fiber fineness as measured by air-flow technique correlated with weight losses in primary (-0.878) and secondary (0.768) peaks.

DISCUSSION

The quality of fiber obtained by dew-, water- and enzyme-retting can be distinct in terms of their color, smell, fineness, handle, and other characteristics. The main reason is because of differences in the activities of the polysaccharide-degrading enzymes involved in each of the three types of retting.^{10,17,18} For example, in dew-retting, pectinases and hemicellulases released by the fungal colonists ret the flax slowly during the 5–8 week retting period. In contrast, water or enzyme retting can be performed relatively rapidly in 3–7 days. The resulting materials showed distinct structural differences especially in water-retted fibers. Quality in

Parameters	UR	DR	ER	WR	SEM (df 11)
Physical					
Handle	+	++	++	+++	
Lustre	+	++	++	+++	
Color	Green	Dark-grey	Greenish-vellow	Pale-vellow	
Fiber fineness (dtex)	65.00	43.51	39.50	32.53	3.24^{*}
Fiber strength (g/denier)	4.93	4.26	3.43	6.20	1.852 ns
Fiber and other fractions (%)					
CWL	31.30	30.18	19.50	25.18	1.63^{**}
ADF	78.45	77.30	85.19	78.79	1.73^{*}
NDF	83.15	85.33	94.06	87.44	1.99^{*}
Cellulose	78.08	75.55	82.02	74.10	0.42^{*}
Hemicellulose	4.70	8.20	8.90	8.70	0.97ns
Lignin	0.37	1.76	1.67	4.69	1.18^{*}
Carbon	41.02	42.25	41.54	42.77	0.316^{*}
Hydrogen	6.18	6.60	6.45	6.45	0.100 ns
Nitrogen	0.27	0.41	0.19	0.28	0.07 ns
Ash	1.34	1.31	0.65	0.50	0.101^{***}
Lipid	1.9	2.61	2.43	2.92	0.12^{*}
Minerals (ppm)					
Ca	67.25	64.85	64.27	67.43	3.36ns
Р	2.66	3.02	1.14	0.87	0.381^{*}
Cu	0.07	0.15	0.11	0.18	0.021 ns
Fe	1.17	4.50	1.36	2.60	0.955 ns
Mn	0.24	0.51	0.14	0.21	0.091^{*}
Mg	10.05	12.55	4.54	5.71	0.744^{***}
Na	4.39	1.09	1.50	0.87	0.248^{**}
K	3.85	9.76	1.37	1.39	0.02^{*}
Zn	0.36	0.33	0.31	0.27	0.017^{*}
DTG parameters					
WL-PP (%)	54.85	61.55	63.91	62.54	1.102^{*}
PT-PP (°C)	341.50	357.80	353.50	355.50	2.02^{***}
WL-SP (%)	31.98	27.22	26.83	26.93	1.287^{*}
PT-SP (°C)	445.30	459.20	442.20	458.70	0.815 ns

Table I	Comparison	of Fiber Ch	aracteristics o	f Unretted,	Dew-,	Enzyme	-, and	Water-retted Fiber	ſS

UR, unretted; DR, dew retted; ER, enzyme retted; WR, water retted. Handle: +, poor; +++, good. Lustre: +, poor; +++, good. CWL, caustic weight loss, WL-PP, weight loss in primary peak; PT-PP, peak temperature in primary peak; WL-SP, weight loss in secondary peak; PT-SP, peak temperature in secondary peak; SEM, standard error of means; df, degrees of freedom. Significant at *, p < 0.05; **, p < 0.01; ***, p < 0.001; ns, not significant.

flax is intricately linked to the proportions of residual pectins, hemicelluloses, lignin, and lipids present in the retted fiber. In the fiber bundles, pectin is deposited mainly in the middle lamella between the fiber and other cells;^{18–21} in contrast, the hemicelluloses are integral components of the fiber cell walls and thereby provide strength. Some of these fractions in the secondary walls are associated with lignin.^{10,11,19} Most of the pectin from the fiber can be hydrolyzed to improve fiber fineness, but, only a limited proportion (nearly 10%) of hemicellulose can be removed during retting or chemical processing without causing reduction in fiber strength. Removal of residual hemicelluloses bound with lignin^{10,20} will reduce fiber strength. Similarly, handle and luster of the fiber were also affected by the retting and processing techniques used.¹⁰ Although the effects of the three retting methods were probably the largest contributor to the variation in physical, chemical, and thermal characteristics of the fiber tested, cultivar differences and growing conditions of the crops in France, Belgium, and Northern Ireland may have affected certain parameters including fiber and inorganic fractions.

Physical characteristics of the fibers, i.e., fineness, strength, color, luster, and handle are key indicators for assessing quality. The positive correlation between fiber fineness and Mg and Ca concentrations shows that finer fibers (i.e., fibers with lower dtex values) contain lower levels of the cations, which are needed to bond pectin and hemicelluloses to the cellulose fibrils. It has been widely reported that fiber fineness, strength, and caustic weight loss are all important factors, which determine fiber quality; that in turn is dependent on the degree of retting, drying conditions of the retted-straw, and the quality of the green straw.^{5,9,10,20} Comparison of physical characteristics and chemical components of two grades of flax straw and the fibers obtained after enzyme retting have shown that the key characteristics, including handle and luster, is dependent on the quality of the straw.²⁰

The pyrolysis and combustion of lignocellulosic components were related to their molecular structure and TG profiles of wood depended not only on cellulose content but also on hemicellulose and lignin.²²⁻²⁴ So as to assess the weight loss and decomposition temperatures of the main constituents of fiber, reference compounds such as cellulose, levoglucosan, hemicellulose, and pectin were analyzed. Pyrolysis of the main component cellulose is preceded by decomposition of pectin and nonstructural hemicellulose, which can be detected as a shoulder to the main primary peak. The pyrolysis of cellulose to levoglucosan in the decomposition band of 200 to 400°C and further decomposition of the residual compounds in the higher band 400 to 600°C have been discussed in detail.²⁵ The rate of pyrolysis of the fiber fractions could be influenced by cations, particularly P, Mn, and K, as some of these minerals could affect peak decomposition temperature.^{7,24} The weight losses in the primary and secondary peaks correlated with caustic weight loss, ADF, NDF, and cellulose showing that the rate of pyrolysis was related to the fiber components. This study, although based on limited sample size, has confirmed the superiority of water-retted fibers compared with the others. Of all the parameters tested, fiber fineness, strength, caustic weight loss, ash, and weight loss in primary peak seem to be important indicators of fiber quality.

REFERENCES

- Butterworth, E.; Elkin, H.A. Linen Industrial Research Institute, Lambeg, UK, Memoir No. 63, 1929; p. 33.
- 2. Turner, A. J. J Text Inst 1949, 40, 857.
- 3. Sharma, H. S. S. Tests Agrochem Cult, supplement to Ann Appl Biol 1986, 7, 114.
- 4. Turner, A. J. J Text Inst 1948, 39, 150.
- 5. Sharma, H. S. S.; Kernaghan, K. Thermochim Acta 1988, 132, 101.
- Crighton, J. S.; Das, A. Thermochim Acta 1979, 29, 319.
- 7. Ramiah, M. V. J. Appl Polym Sci 1970, 14, 1323.
- Cabradilla, K. E.; Zeronian, S. H. In Thermal Uses and Properties of Carbohydrates and Lignins; Safizadeh, F.; Sarkansen, K. V.; Tillman, D. A., Eds.; Academic: New York, 1976.
- 9. Turner, A. J. Quality in Flax; Lambeg Industrial Research Association, Belfast, UK, 1954.
- Sharma, H. S. S.; van Sumere, C. The Biology and Processing of Flax; M Publications: Belfast, UK, 1992.
- 11. Sharma, H. S. S. Int Biodeter 1987, 23, 181.
- Anonymous. British Standard Handbook, BS No. 3982, 1974. 13Sharma, H. S. S.; Gilmore, C. Text Inst 1989, 80, 285.
- 14. Van Soest, P. J.; Wine, R. H. J Assoc Agri Chem 1967, 50, 50.
- Christian, K. R. Field St Rec CSIRO: Australia 1971, 10, 29.
- Anonymous. Official Standardised and Recommended Methods of Analysis; The Society of Analytical Chemistry, Heffers Printers Ltd.: Cambridge, 1973.
- Sharma, H. S. S.; Faughey, G.; McCall, D. J Text Inst 1996, 87, 249.
- McDoughall, G. J.; Morrison, I. M.; Stewart, D.; Weyers, J. D. B.; Hillman, J. R. J Sci Food Agric 1993, 62, 1.
- Morvan, O.; Januneau, A.; Morvan, C.; Demarty, M.; Ripoll, C. Ann Appl Biol 1988, 112, 107.
- Van Sumere, C. F.; Sharma, H. S. S. Aspects Appl Biol 1992, 28, 15.
- Akin, D. E.; Morrison, W. H., III; Gamble, G. R.; Rigsby, L. L.; Henriksson, G.; Eriksson, K. L. Text Res J 1997, 67, 279.
- 22. Beall, F. C. Wood Sci 1972, 5, 102.
- Cardwell, R. D.; Luner, P. Adv Chem Ser 1977, 164, 362.
- 24. Hirata, T.; Abe, H. Mukugzai Gakkaishi 1973, 19, 451.
- Sekiguchi, Y.; Frye, J. S.; Shafizadeh, F. J Appl Polym Sci 1983, 28, 3518.