Determining Fiber Fineness in Flax Using Derivative Thermogravimetric Analysis, Scanning Electron Microscopy, and Airflow Methods

G. J. FAUGHEY,[1] S. S. SHARMA,[1,2] R. D. MCCALL[1,2]

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

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

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ABSTRACT: This study investigates the assessment of fiber fineness by a range of techniques. Conventional airflow and gravimetric methods were compared with derivative thermogravimetric analysis (DTG). The novel use of scanning electron microscopy (SEM) for examining fiber cross-sections has also been deployed. DTG analysis when compared with airflow measurements has shown that differences in fiber fineness can be modeled from the pyrolysis data. The relationship between the two methods was highly significant. The diameter of the fiber cross-sections, measured from SEM micrographs, revealed a significant relationship with both DTG and airflow measurements. Gravimeteric determinations exhibited a poor correlation with the other methods and have shown an inability to distinguish between fibers of similar grades. The use of DTG for predicting fiber fineness was validated using partial least squares regression on a test set of samples. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 508–514, 2000

Key words: derivative thermogravimetric analysis; scanning electron microscopy; airflow; flax; fiber fineness

INTRODUCTION

Scutched flax comprises long, coarse fiber strands, which are groups of fiber bundles, and each strand consists of several hundred ultimate fibers cemented together by pectins and other noncellulosic polysaccharides.[1, 2] It is the ability of these fibers to split up through hackling, spinning, and the processes in between, which contribute to the count or lea of a yarn.[3] The determining factors are degree of retting, fiber components, mechanical processing, chemical processing, and others.[3–5]

Fiber fineness has long been considered an important characteristic of flax,[6,7] however being a compound fiber, the determination of fiber fineness is operator dependent and is difficult to obtain by means of gravimetric method.[8] The most frequent method of evaluation is by organoleptic assessment, which is highly subjective. Currently the airflow method provides the best measurement of fiber fineness. It is a tedious and operator-dependent technique.

Microscopic methods have proven unsuccessful for a variety of reasons, most commonly because they are long winded. However, the development of a rapid preparation technique that allows the clean observation of flax fiber cross-sections with-

Correspondence to: G. J. Faughey.

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out embedding media may provide a useful indication of fiber fineness. The area of flax fiber cross-sections has long been of interest,[7,9] and it is envisaged that this could provide a comparatively accurate and reproducible assessment of fiber fineness.

Derivative thermogravimetry (DTG) can also be used to investigate differences in flax fibers. Previous research by Sharma and Kernaghan[10] has shown that DTG can reveal changes during different stages of processing. The use of this technique for detecting differences in fiber grades was reported by Sharma et al.[11] The results of this confirmed that particle size of the test sample could affect the pyrolysis pattern due to differences in surface area and heat conductivity. Fine flax fibers have a greater surface area compared with coarse fibers for the same weight, assuming that density between the fibers is not dissimilar. In addition the effects of chemical treatments on flax fiber have also been investigated using this method.[12]

The aims of this investigation were to identify the relationships between fiber fineness determinations by DTG analysis, airflow, scanning electron microscopy (SEM), and gravimetric methods, to predict fiber fineness using partial least squares (PLS) regression analysis and to develop a rapid and reliable technique for detecting fiber fineness.

MATERIALS AND METHODS

Fiber Samples

The reference fibers of different grades used in this study were obtained from the Institute of Textiles in France (Villeneuve). Other samples included were received from Holland, Poland, and North Ireland as part of a comprehensive research program on fiber quality. All samples had been hackled prior to assessment.

Conditioning and Test Atmosphere

The samples were conditioned and assessed in the standard atmosphere for testing textiles,[12] i.e. an atmosphere of relative humidity 65 ± 2% and a temperature of 20 ± 2°C.

Airflow Meter

Bundles of flax fibers with a length of 8 cm and a mass of 2.6 g were taken at a representative place from the flax bundle.[13] A higher mass (3.0 g) was used for coarse samples so that a reading could be obtained. Calibration equations for establishing the relationships between airflow measurements using 2.6- and 3.0-g masses were developed. This was necessary, as coarse samples cannot be assessed using a 2.6-g mass. The fibers were fluffed to break up any lumps before being inserted into the cylinder, and measurements of air permeability were recorded on the scale reading. The readings were then converted to the required units. A minimum of 10 measurements was carried out on each of three subsamples.

Gravimetry

After careful subsampling, several sections of fiber all 80 mm long were cut using serrated scissors. From these a total of 100 fiber bundles per sample were carefully extracted and weighed under the appropriate conditions.[14] From the measurements obtained, d/tex and denier were calculated.

Thermogravimetric Analysis

Thermogravimetric analysis of the fiber samples was determined at a heating rate of 20°C/min and an air flush rate of 10 ml/min. All samples were prepared by cutting to a particle size of < 1 mm using a pair of serrated scissors. A representative sub sample weighing 3.1–3.2 mg was used for each test. Each sample was analyzed three times.[11] The DTG curve and the TG weight loss data were calculated using Graphware (Mettler, Toledo). The primary decomposition peak extends from 240–400°C, a minor peak follows this from 400–520°C. The changes in weight losses and decomposition temperatures in the two ranges were analyzed. To help identify the fiber constituents, a number of reference materials, including cellulose (Sigma, C-8002), (C-4888), araban (Koch-light, 0444-00), Na-polypectate (P-1879), amylopectin (A-8515), levoglucosan (A-8417), and lignosulphonic acid (Aldrich, 37097-5), were also analyzed by DTG.

Scanning Electron Microscopy

Subsamples of the flax fibers were fractured under liquid nitrogen using cooled scissors.[15] The stub and sample were removed from the liquid nitrogen and allowed to warm up to ambient temperature. The sample in the stub was then sput-

Table I Comparison of the Range of Measurements by Airflow (d/tex), DTG Analysis (Peak 1, Weight Loss %), Gravimetric Analysis (Denier), and SEM Methods (μm)

Method	n	Minimum	Maximum	Mean
DTG	25	58.08	65.66	61.64
Airflow	25	23.45	83.00	54.63
SEM	25	1.89	5.36	3.50
Gravimetry	25	26.10	93.83	54.30

ter coated with platinum, and transferred to the specimen chamber of a JEOL 35CF SEM. The accelerating voltage in the SEM was kept to a maximum of 10 kV in order to minimize charging effects. A series of 10 micrographs per sample were taken at a magnification of 200 times. From these measurements of 50 fiber cross-sections per sample were taken.

Statistical Analysis

All statistical analyses were carried out using the "Unscrambler" developed by Computer Aided Modelling (CAMO) Norway. PLS modeling procedures were used to develop relationships between the physical or chemical properties of the investigated fiber samples.

RESULTS

Airflow Meter

Calibration of the airflow meter was performed to a high degree using eight reference samples from the Institute of Textiles in France (Villeneuve). Airflow measurements on the long fiber have indicated differences in the fiber samples with d/tex values ranging from 23–83 (Table I).

Derivative Thermogravimetric Analysis

The thermal spectra of the fiber samples (26) were significantly different for both fiber type and also fiber fineness. Higher weight loss in peak 1 (64–66%), representing cellulose decomposition, was characteristic of fine fibers compared with a lower weight loss (58–61%), associated with coarser samples (Table I); this corresponded with earlier reports.[11] Differences in the primary peak temperatures were also evident, ranging from 346–352°C. Lower peak 1 temperatures were observed in samples with a higher peak 1 weight loss (Table II).

Gravimetric Analysis

The evaluation of fiber fineness by gravimetric analysis has shown d/tex values extending from 26.1–93.83 (Table I). At the finer end of the scale fibre grading was similar to that derived from DTG and airflow methods, however at the mid- to high range the accuracy of the method was significantly reduced. At the sample preparation stage a high degree of interfiber and intrafiber variation was observed regarding fiber bundle diameter.

Scanning Electron Microscopy

SEM micrographs revealed fiber cross-section diameters ranged between 1.89 and 5.36 μm (Table I). Considerable variation in fiber bundle diameter between samples was evident (Figure 1a,b). The polygonal shape of the fibers coupled with the visible presence of the lumen provided a clear indication that the measurements were accurate representations and not exaggerated by shearing

Table II Comparison of Fine, Medium, and Coarse Flax Fibers Using DTG Parameters

Fiber Grade	Peak 1 Weight Loss	Peak 1 Temp. °C	Peak 2 Weight Loss	Peak 2 Temp. °C	Residue (Ash Content) (%)
Fine	65.51	344.40	25.44	428.48	1.00
Medium	61.29	350.48	28.70	435.46	1.67
Coarse	58.61	352.56	31.06	452.37	1.28
SEM	0.034***	1.687*	0.375***	2.490***	0.482ns

Standard error of the mean (SEM), significant at $*P < 0.05$; $**P < 0.01$; $***P < 0.001$; ns, not significant.

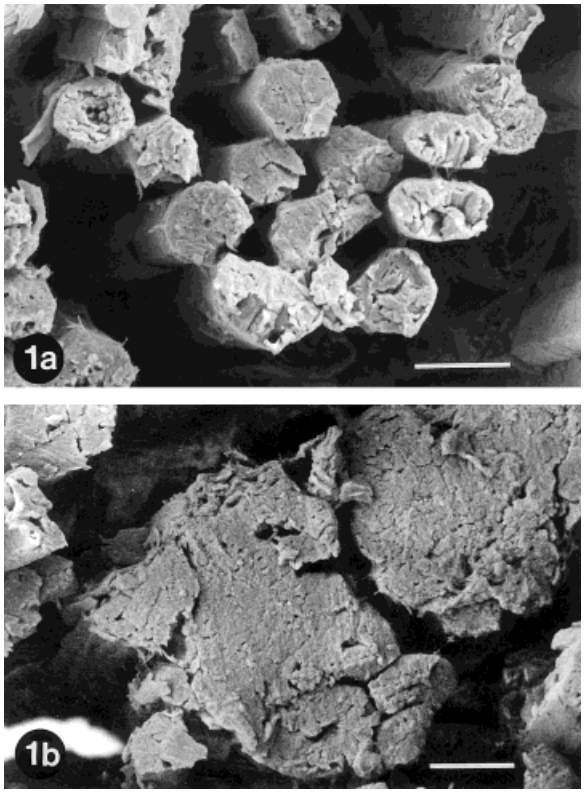


Figure 1 SEMs of fine (a) and coarse (b) flax fibers, showing the presence of noncellulosic polysaccharides cementing the fiber bundles (b). (Bars represent 20μ(m).

the fibers during preparation. There were no obvious differences in the form of the fiber cells, which could be related to fiber fineness. Although no measurements were made, it would appear that the average number of fiber cells that constitute a fiber bundle might well be related to determinations of fiber fineness.

Statistical Correlation's between DTG, SEM, and Gravimeteric Analysis with the Airflow Reference Method

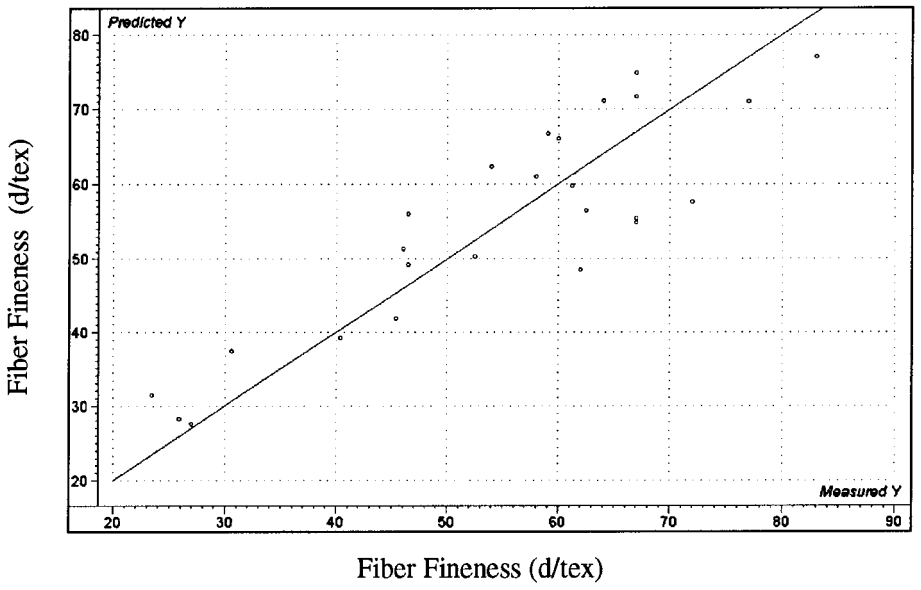
The airflow method has shown a highly significant negative correlation with DTG and a positive correlation with SEM, determinations of fiber fineness with r^2 values of 0.90 for both. The r^2 values for predictions were slightly lower at 0.84 and 0.89 respectively (Table III). The accuracy of the relationship was reduced at high d/tex values (Figure 2a,b). Gravimeteric determinations did not correlate well with the other methods, however a weak correlation was observed between gravimetric assessments on the fiber set and airflow measurements (Table III). The relationship between DTG and SEM methods was also significant (Table III).

Statistical Validation of the Methods

The raw data obtained from these experiments has not been preprocessed by any mathematical treatment. Of the three methods, gravimetry, DTG, and SEM, the latter two have shown to be accurate at predicting reference measurements made using the airflow. The mean deviations for DTG and SEM determinations were 2.08 and 2.31, respectively (Table IV), the prediction set included 11 samples for DTG and 6 for SEM. The mean DTG deviation appears to be significantly increased in sample 11 (Table IV), which is an SO_2-treated coarse fiber, indicating that the model is stressed at high d/tex values. Gravimetric predictions exhibited a high mean deviation of 5.58 and considerable variation between individual predictions in the sample set (6) was evident regardless of d/tex rating (Table IV).

Table III Calibration and Prediction Statistics of DTG Analysis, SEM, Airflow and Gravimetric Methods Showing Standard Error of Calibration (SEC), and Standard Error of Prediction (SEP)

Methods	n	SEC	R^2	SEP	R^2
DTG and SEM	25	0.57	0.76	0.54	0.72
DTG and Airflow	25	7.49	0.90	7.02	0.84
DTG and gravimetry	25	14.58	0.47	13.45	0.32
Gravimetry and Airflow	25	13.09	0.65	12.20	0.58
Gravimetry and SEM	25	0.62	0.72	0.57	0.66
SEM and Airflow	25	6.82	0.90	7.28	0.89



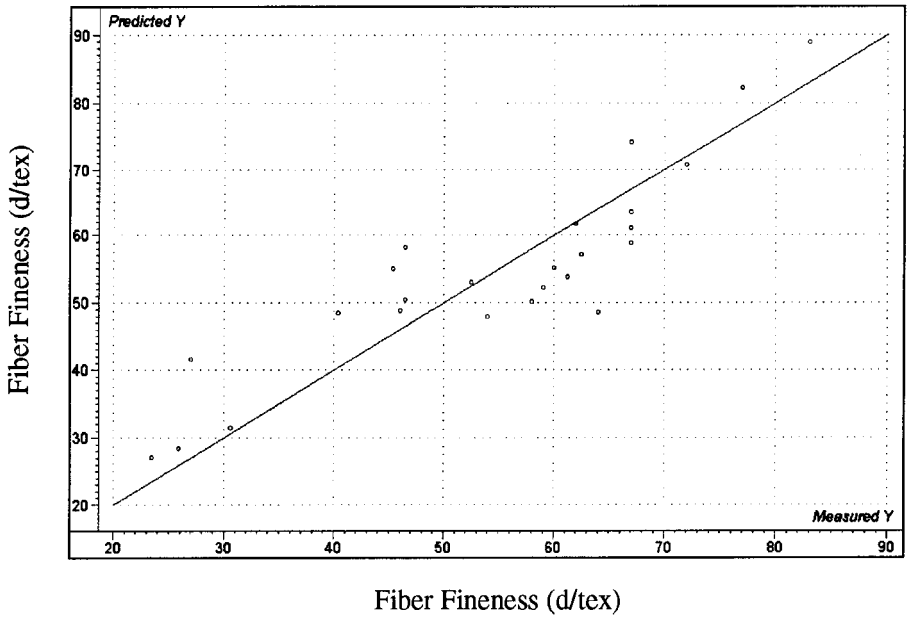


Figure 2 (a) Correlation of DTG analysis peak 1 weight loss and airflow method d/tex units, using PLS regression analysis. Calibration $r^2 = 0.90$; Validation $r^2 = 0.84$; n = 25. Standard error of prediction 7.02. (b) Correlation of airflow (d/tex) and SEM measurements (μm) of fiber fineness, using PLS regression analysis. Calibration $r^2 = 0.90$; Validation $r^2 = 0.89$; n = 25. Standard error of prediction 7.28.

Table IV Validation of the Prediction Equations of DTG Analysis, SEM, and Gravimetric Methods for Determining Fiber Fineness as Measured by the Airflow Reference Method

Method	Sample	Airflow	Predicted	Deviation
DTG	1	49	44.84	2.21
	2	75	68.31	2.41
	3	48	43.91	2.26
	4	51	56.94	2.00
	5	40	48.03	2.09
	6	45	32.67	2.95
	7	46	48.30	2.09
	8	48	57.61	2.01
	9	46	45.97	2.17
	10	37	44.84	2.21
	11	87	102.90	5.20
Mean		52	54.03	2.31
SEM	1	49	54.87	1.94
	2	75	64.01	2.14
	3	48	51.89	1.96
	4	51	57.51	1.96
	5	40	48.37	2.03
	6	45	39.05	2.45
Mean		51.33	52.62	2.08
Gravimetry	1	49	188.81	13.51
	2	75	60.133	2.06
	3	48	52.62	1.99
	4	51	142.40	8.97
	5	40	93.05	4.32
	6	45	72.10	2.64
Mean		51.33	101.51	5.58

DISCUSSION

The results of fiber fineness determinations by DTG and airflow methods suggest that differences in fiber fineness can be modeled and subsequently predicted from the weight loss data in the primary decomposition band. The relationship between the two methods was highly significant, indicating that DTG could replace the airflow method of determining fiber fineness.

One of the characteristics of poor-quality fiber is its inability to split up into fine strands during the preparation and spinning processes; this is due to the presence of a high proportion of noncellulosic materials, which bind the fibers together.[16–18] It is commonly known that quality in flax is partially determined by the levels of these components.[5] The role of the residual fractions determining quality has been widely investigated.[6] DTG analysis suggests that weight loss and the pyrolysis thermogram can detect differences in other quality characteristics of fibers.

The results in Table II indicate the sensitivity of DTG peak temperature and weight loss to identify subtle differences in fibre fineness. Higher peak 1 weight loss corresponded with lower peak 1 temperatures. This may suggest that samples with higher cellulose content and therefore proportionally less hemicellulose and pectin allow pyrolysis to take place in a narrower temperature band. Additionally the peak temperature of reference samples such as cotton wool will take place nearer 340°C (unpublished work). DTG is reliable and reproducible, and other aspects of fiber and yarn qualities can be quantified from the thermal spectra.[10, 11]

SEM measurements revealed a highly significant correlation with DTG and airflow methods. The improved method of fiber preparation prior to mounting in the SEM allows undistorted images

to be taken.[15] The method is certainly quicker than previous microscopic attempts and provides a direct measurement of fiber fineness; however it is still a lengthy and expensive process.

Gravimetric analysis did not prove to be a successful method of determining differences regarding fiber fineness. The reason for its inaccuracy could partly be due to its operator dependence, which means the method is highly subjective. Perhaps of more importance is that this method assumes density between the samples is not dissimilar. The results contradict this hypothesis. Cellulose chemistry is such that accurate determinations of molecular weights are difficult to obtain and are dependent on the method used.[19] In addition the deposition of other matrix polysaccharides, hemicellulose and lignin, is highly irregular on flax fiber. Therefore this method alone cannot with any degree of accuracy provide an estimation of fiber fineness unless some account of fiber fractions are considered.

Subjective assessments of flax fiber currently determine the price paid for any batch. Any inaccuracy occurred in making this valuation is carried by the spinner and ultimately the consumer. We are in no doubt that a replacement objective method of classification will lead to marketable improvements in processing. The difficulty arises in developing a method that can operate with the speed required, while revealing much about the fibers characteristics. To date little development has occurred in test methods for flax fibers, yarns, and fabrics and few have been standardized. Nevertheless, as processing conditions are geared towards better quality at maximum output, an optimal quality of fibers is required for the industry.[8] The industry needs test methods that can rapidly and accurately determine fiber characteristics. This requirement can only be met by continued research into the fiber properties, which determine fiber and fabric characteristics.

This study although based on a small sample set, has shown a significant relationship between DTG weight loss and airflow measurements. Currently, work is in progress to expand the database in order to improve the prediction accuracy. The development of modern instrumental methods such as derivative thermogravimetric analysis and near infrared spectroscopy[20] for accurate determination of fiber properties, could allow further understanding of the inherent peculiarities in flax.

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