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Correlating the Fineness and Residual Gum Content of Degummed Hemp Fibres

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Abstract: It is well known residual gum exists in degummed or retted hemp fibres. Gum removal results in improvement in fibre fineness and the properties of the resultant hemp yarns. However, it is not known what correlation if any exists between the residual gum content in retted hemp fibres and the fibre fineness, described in terms of fibre width in this paper. This study examined the mean width and coefficient of variation (CV) of fibre width of seventeen chemically retted hemp samples with reference to residual gum content. The mean and CV of fibre width were obtained from an Optical fibre diameter analyser (OFDA 100). The linear regression analysis results show that the mean fibre width is directly proportional to the residual gum content. A slightly weaker linear correlation also exists between the coefficient of variation of fibre width and the residual gum content. The strong linear co-relation between the mean of fibre width and the residual gum content is a significant outcome, since testing for fibre width using the OFDA is a much simpler and quicker process than testing the residual gum content. Scanning Electron Microscopy (SEM) reinforces the OFDA findings. SEM micrographs show a flat ribbon like fibre cross-section hence the term "fibre width" is used instead of fibre diameter. Spectral differences in the untreated dry decorticated skin samples and chemically treated and subsequently carded samples indicate delignification. The peaks at 1370 cm^{-1}, 1325 cm^{-1}, 1733 cm^{-1}, and 1600 cm^{-1} attributed to lignin in the untreated samples are missing from the spectra of the treated samples. The spectra of the treated samples are more amine-dominated with some of the OH character lost.

Keywords: Hemp, Residual gum content, Optical fibre diameter assessment, Fibre fineness, Chemical retting

Introduction

Beside cellulose the hemp fibre consists of hemicellulose, lignin, pectin and other mixtures that bind fibres together. The levels of these impurities greatly impact on the properties of the fibre.

When all of the impurities such as the hemicelluloses, lignin's and pectin's are removed the fibre is separated into its individual form. The hemp fibre in its individualised form is 10 to 51 μm in width and 5 to 55 mm in length. The most effective ways of reducing the fibre into its individual form are chemical retting[1-9], steam explosion[6,10,11], ultrasonic retting[6] and biological retting[5,6,8,9,12-15]. Chemical and biological retting are commonly used for fibre extraction whereas the other two methods are still in the developmental stages.

Chemical retting of hemp is a rapid process compared to that of biological retting. Chemical retting involves the soaking of the hemp bark in aqueous alkaline solutions. Alkalis such as sodium hydroxide, potassium hydroxide and sodium carbonate are commonly used. The retting is generally conducted at elevated temperatures for durations of one to four hours. A detergent is used to help accelerate the penetration of the alkali into the fibre bundles. Hurren *et al.*[3] evaluated the efficiency of degumming hemp fibres with different chemical retting recipes used for other bast fibres.

Biological retting uses enzymes and bacteria in aqueous solutions to separate the fibre bundles. Batching is conducted at ambient temperatures for one to two days. Biological retting is not as efficient as chemical retting and sometimes needs to be followed by a mild chemical retting to enable efficient fibre separation. The biological systems need to be closely monitored as some enzymes and bacteria can damage cellulose leading to a deterioration of fibre properties.

Colour is dependent on the system of extraction from the bark with colours varying from yellowish, greenish, brownish to grey. The base colour of the fibre can lead to problems in dyeing pastel or bright shades. The colour of the fibre has a relationship with the fibre separation with whiter colours achieved as the degree of separation increases. It was found by Hurren *et al.*[3] that residual gum and lignin have a large influence on fibre colour.

With either method it is important to establish the degree of fibre separation. Inefficient separation leads to poor quality yarn and fabrics. The traditional methods for establishing fibre separation are the Fried test[15], FTIR spectroscopy[13, 14,16] and residual gum content[6,8,9,17].

The Fried test has been used in several papers for the analysis of the degree of retting of flax fibre. It looks at the degree of separation of the fibres after retting. A group of slides showing degrees of separation are used and compared to the results obtained during the retting process. This method is very subjective and does not account for systems that show a better degree of separation than the slides.

FTIR spectroscopy has been used mainly for the research analysis of the degree of retting. Functional groups associated with gums, lignins and waxes can be identified and quantitatively analysed. This method requires very accurate

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and expensive analysis equipment and takes considerable time and experience to undertake. These constraints limit its use to research applications.

The residual gum content test was used by Das Gupta *et al.*[17] in 1976. The test uses a series of caustic degumming to dissolve out any of the residual gum left in the fibre. The residual gum is then expressed as a percentage of the original fibre mass. The test presumes that the more gum removed the better the fibre separation. Unfortunately the test takes considerable time to conduct, which limits its use for industrial analysis applications.

A new system for analysing fibre separation is by measurement of the mean fibre width of the retted fibre. Optical fibre diameter analysis (OFDA) measures the width of the fibre snippets by the use of a projection microscope and a digital camera. A determined number of snippets are measured during each test and the mean and coefficient of variation (CV) are calculated using the system software. The test can be conducted in about one minute with minimal sample preparation time. These results can then be correlated with the residual gum content of the hemp fibre specimen.

OFDA is a direct method of evaluating the fibre separation as mean and CV of width can be directly related to the fineness and evenness of a yarn produced[3]. Fibre separation has been quoted in terms of residual gum content in most literature on bast fibres. This paper looks at the correlation between residual gum content and fibre mean width and CV of fibre width. Correlation of these two factors would enable quick evaluation of the degree of fibre separation, the residual gum content, and the fineness of the degummed hemp and other bast fibres.

Experimental

Materials

The hemp variety Zolotonshka (Ukraine) was sourced from plant lots grown by Fibrenova in 2000. The plants were decorticated dry using a decorticator specially designed by Fibrenova. Chemical retting was conducted in the presence of sodium hydroxide, sodium carbonate and an anionic wetting agent (Albegal FFA^{TM}). Variations were made in the amounts of sodium hydroxide (0.125-2.0 %) and sodium carbonate (0.0-2.0 %) used to obtain variations in the degree of retting. A total of 17 trials were conducted. The sodium hydroxide (NaOH) and acetic acid (CH_3COOH) were sourced from Redox Chemicals Pty Ltd. Hydrochloric acid (HCl) was sourced from Vival Chemicals Pty Ltd. All of the chemicals used for the processing of the trials were of an industrial grade.

Residual Gum Content Evaluation

For each of the 17 trials, six test specimens of 3 g each were randomly selected from the chemically retted hemp samples. The method of analysis of residual gum content was as per Das Gupta *et al.*[17].

Fibre Width Measurement

The OFDA instrument was used to measure the width of retted hemp fibres. Five OFDA tests were conducted for each of the trials. The test specimens were selected by zoning and random sampling from each of the chemically retted hemp samples. Each test consisted of the measurement of 4000 fibres. The mean and CV of width were calculated using the statistical software on the OFDA. The average of the five measurements was tabulated and used for the comparisons.

SEM and FTIR Examination

The surface features of degummed hemp fibres were examined by scanning electron microscopy (SEM). SEM was conducted on the raw skin samples of the Ukraine variety, the chemically retted fibre of trial 4 and fibre subsequent to the removal of residual gum in trial 4.

FT-IR spectroscopy experiments were conducted to reveal the different characteristics of hemp skins and the changes that occur in the compositions upon chemically retting. A Perkin Elmer FT-IR 2000 spectrometer with a vertical ATR was used. Region from 750 cm^{-1} to 4500 cm^{-1} was scanned, with 132 scans employed to remove the water peaks from the spectra.

Results and Discussion

SEM Results

The SEM results have been given in Figures 1, 2, and 3. Figure 1 is an end on shot of the decorticated bark that has not undergone any natural or chemical retting. As is expected the fibres are still glued together into tight bundles. Figure 2 shows the fibres that have been chemically retted. This slide displays a degree of fibre separation however there are still bundles of fibres present. The OFDA measurements for these fibres show that the mean fibre width is 22.16 μm

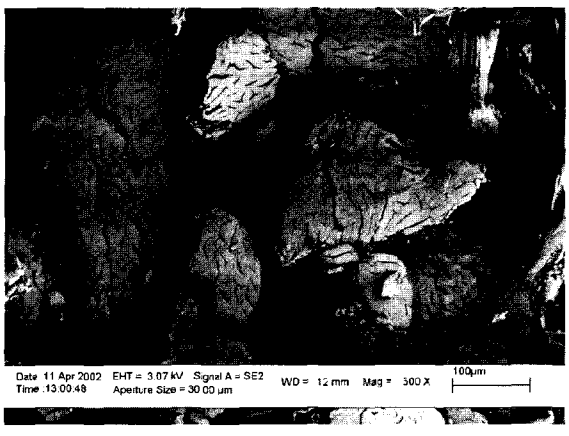

Figure 1. Decorticated unretted "Ukraine" bark.

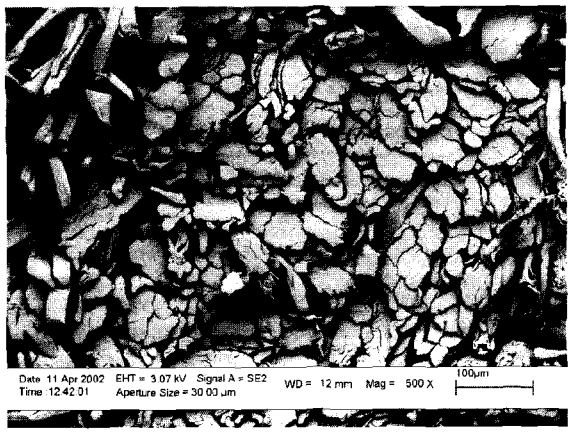

Figure 2. Chemically retted fibre (trial 4).

Figure 3. Fibres after Das Gumpta *et al.* residual gum test (trial 4).

and a CV of fibre width of 72.18 % (see Table 1, trial 4). The CV of the fibre is still very high and this can be explained by the bundles of fibres still present in the sample shown by the SEM.

Figure 3 reveals the fibres after the further removal of residual gum. This SEM micrograph shows a far larger degree of fibre separation than the two previous slides. The OFDA measurements for these fibres show that the mean fibre width is 18.36 μm and a CV of fibre width of 61.2 %. The mean fibre width has decreased compared to that of the chemically retted fibre. The CV of the fibre has also reduced when compared to the chemically retted fibre sample. Although the CV has reduced it is still considered large for a natural fibre. This large CV could be explained by the fibre bundles still present in the fibre sample. The fact that some fibres are still bound together also suggest that the removal of the residual gum is incomplete using the Das Gupta *et al.* method[17].

Correlation Analysis of Fibre Width and Residual Gum Content

Table 1 display the results of the OFDA measurements

Table 1. Fibre width and residual gum test results

Trial	OFDA fibre width results		Residual gum content results	
	Mean (μm)	CV (%)	Mean (%)	St. dev.
1	22.54	71.02	16.40	0.192
2	23.73	74.26	17.43	0.327
3	22.93	72.14	15.76	0.430
4	22.16	72.18	12.72	0.611
5	21.22	68.34	12.24	0.064
6	22.39	74.18	11.14	0.553
7	22.28	76.13	11.71	0.280
8	21.66	71.56	7.50	0.216
9	21.05	71.30	6.48	0.581
10	20.47	69.00	6.96	0.311
11	21.29	69.94	5.38	0.136
12	20.13	64.28	6.02	0.326
13	20.24	63.30	5.00	0.408
14	20.68	67.62	4.18	0.101
15	19.62	63.42	3.37	0.131
16	19.47	63.52	2.64	0.125
17	19.68	64.12	2.12	0.095

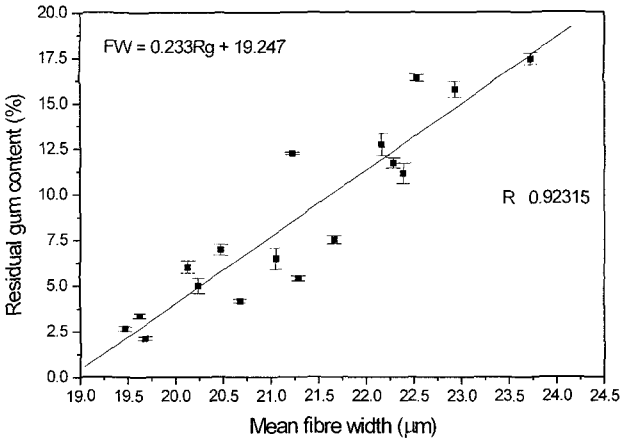

Figure 4. Residual gum content versus mean fibre width.

conducted on the chemically retted fibres and of the residual gum content trials on the chemically retted hemp fibres. Fibre width and coefficient of variation of width are recorded as an average of five tests conducted. Residual gum content results tabled are the average of the six tests that were carried out for each of the trials. The standard deviation of the six values has also been given.

Linear regression was conducted on the results of the fibre width measurements with reference to the residual gum content (*Rg*) results. Linear regression was conducted on both the mean fibre width and the coefficient of variation of width. Figure 4 shows the plot of the residual gum content versus the mean fibre width. Figure 5 shows the plot of the residual gum content versus the coefficient of variation (*CV*)

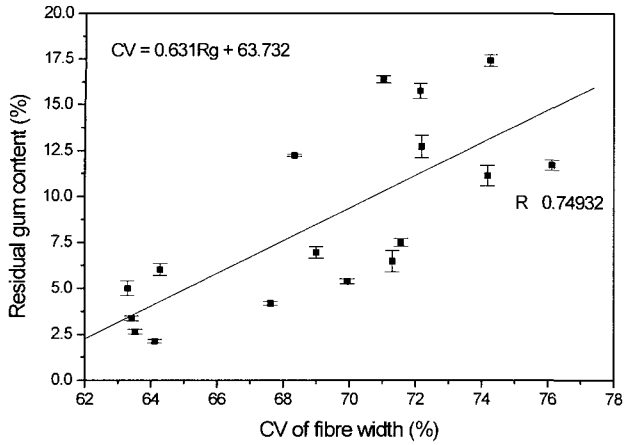

Figure 5. Residual gum content versus coefficient of variation of fibre width.

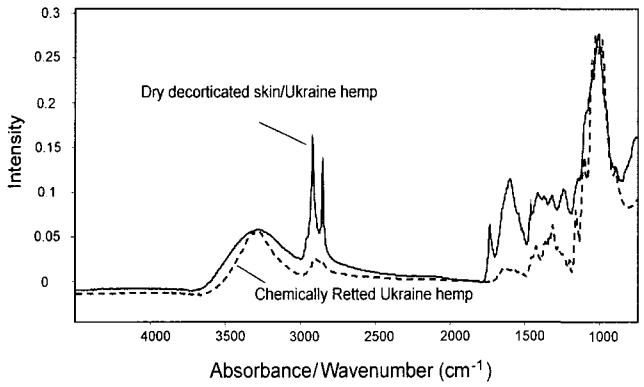

Figure 6. Overlaid representation of the FT-IR spectra of dry decorticated skin and chemically retted Ukrainian Hemp samples.

of width. The regression lines are fitted to the relationship between the mean fibre width (*Fw*) versus residual gum content and coefficient of variation versus residual gum content respectively. The linear regression equations were checked using the correlation coefficient (*r*). The correlation coefficients given in Figure 4 and Figure 5 show significant correlation between the residual gum content and the mean fibre width (r = 0.923) and CV of fibre width (r = 0.749).

FT-IR Results

FT-IR spectra of the dry decorticated skin and the chemically retted samples from the Ukrainian hemp variety are studied. The peak assignments on the dry decorticated samples and the spectral changes that occurred after chemical retting are discussed. Figure 6 shows the overlaid representation of the FT-IR spectra of dry decorticated skin and the chemically retted samples. The spectrum of dry decorticated hemp is dominated by alcohol and ether peaks occupying 1200 to 800 cm^{-1} region.

All the peaks were normalized to the ether peak (R-O-R)

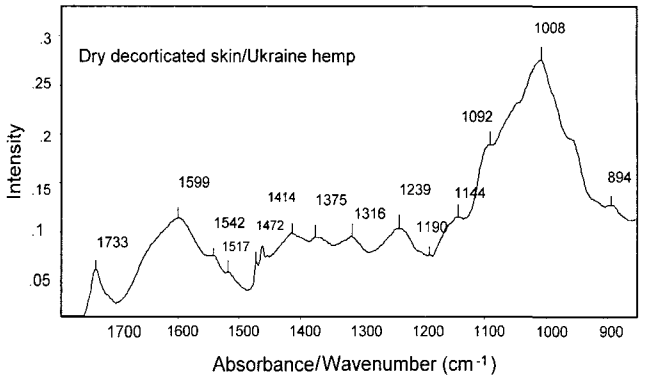

Figure 7. FTIR spectrum of the dry decorticated skin sample at in the 850 cm^{-1} to 1800 cm^{-1} region.

around 1008 cm^{-1} (Figure 6), which is attributed to the epoxide (cyclic ether) in cellulose. In the spectrum of dry decorticated hemp O-H bands seem to mask N-H bands. The more detailed view of the FTIR spectrum of the dry decorticated skin sample in the 850 cm^{-1} to 1800 cm^{-1} region can be seen in Figure 7. The bands at 1370 cm^{-1} and 1325 cm^{-1} are due to the bending vibration of the phenolic OH group in Lignin. The peak at 1733 cm^{-1} of the dry decorticated sample is attributed to carboxyl groups (C=O) resulting from oxidation of aromatic rings of lignin (Figure 7). The low intensity of this peak suggests that it is due to the oxidation of the lignin.

In the spectrum of the chemically retted sample (Figure 6, dotted spectrum) a more amine-dominated spectrum with two peaks at 3329 and 3275 cm^{-1} is seen with some of the OH character lost. One of the most significant differences between these two samples is the reduction in the intensities of the alkyl peaks (C-H stretch) at 2916 and 2848 cm^{-1}. Some alkanes are lost as part of a compound as a result of the chemical retting (See 2 sharp peaks at 2848 and 2916 cm^{-1} and a smaller one around 2950 cm^{-1} in the spectrum of the dry decorticated sample). This can be seen in the overlaid representation. Another significant change is the loss of the carbonyl peak at 1733 cm^{-1}. This may also be attributed to the reduction in lignin concentration. The C=O peak at 1733 cm^{-1}[16] is significant in decorticated skin samples but very weak and unresolved in the chemically retted sample (Figures 6 and 7). The 1600 cm^{-1}[18] peak which was attributed to aromatic C=C stretch in lignin and 1505 cm^{-1} peak arising from the skeletal vibrations of the aromatic rings in lignin are absent in the spectrum of the chemically retted hemp. Another set of peaks often used in the diagnosis of delignification are alkyl peaks at 2920 and 1460 cm^{-1}. Both of these peaks existed in the spectrum of the untreated decorticated sample but do not exist in the spectrum of the chemically retted specimen, suggesting delignification.

The lignin content could be estimated based on the combined areas of these peaks at 1506 cm^{-1} (attributed to the

C-H vibrations of the aromatic ring) and 1471 cm^{-1} (attributed to asymmetric C-H deformation in the lignin). Again, these peaks -though not very intense- are present in the spectrum of untreated sample but absent from the spectrum of the chemical retted sample indicating delignification. 1460 cm^{-1} region is occupied by CH, CH_2, CH_3 bending modes, which could be due to methoxyl, also seems to be lost in the treated specimen.

One of the main constituents of the gum is lignin. Lignin, found in the lamella, primary and secondary wall, is a natural polymer that acts to bind the fibrous hemp together. Figure 6 shows an overlay of the dry decorticated skin and the chemically retted fibre. The dry decorticated skin posses a high lignin content which is reinforced by the SEM image (Figure 1) that shows strong binding of the fibres in the skin. The reduced peak of the chemically retted fibre shows that delignification has been achieved through the depolymerisation of the lignin during chemical retting process (Figure 6). This is confirmed by the SEM image (Figure 2) which shows large degree of fibre separation. Delignification is therefore a major influence in regards to optimising fibre individualisation and therefore a factor that impacts on both fibre width and coefficient of variation.

Conclusions

This paper examined the correlation between the residual gum content and the width of chemically retted hemp fibres. The results show that there is an approximately linear correlation between the residual gum content and fibre width as measured on the Optical fibre diameter analyser (OFDA). This was also the case with the coefficient of variation of fibre width. The significance of these findings is that the tedious evaluation of residual gum content of retted bast fibres may be replaced by the much faster measurement of fibre width using an Optical fibre diameter analyser.

The SEM results indicate that the residual gum content test procedures used can not completely remove the residual gum and some un-separated fibre bundles still exist in the specimens after the test.

The spectral differences in the untreated dry decorticated skin samples and chemically treated and subsequently retarded samples indicate delignification. The peaks attributed to lignin in the untreated samples are missing from the spectra of the treated samples.

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References

1. H. M. Wang, R. Postle, R. W. Kessler, and W. Kessler, *Proceedings of the International Conference-Bast Fibrous Plants on the Turn of Second and Third Millennium*, Shenyang, China (2001).
2. C. Tofani and B. Ceschi, *Proceedings of the International Conference-Bast Fibrous Plants on the Turn of Second and Third Millennium*, Shenyang, China (2001).
3. C. J. Hurren, X. Wang, H. G. S. Dennis, and A. F. K. Clarke, *82nd Textile Institute World Conference*, Cairo, Egypt (2002).
4. A. Keller, M. Leupin, V. Mediavilla, and E. Wintermantel, *Industrial Crops and Products*, **13**, 35 (2001).
5. P. Bel-Berger, T. Von Hoven, G. N. Ramaswamy, L. Kimmel, and E. Boylston, *The Journal of Cotton Science*, **3**, 60 (1999).
6. M. Leupin, *Hemp, Flax and Bast Fibrous Plant Symposium*, Poznan, Poland, 119 (1998).
7. W. H. Morrison III, D. E. Akin, G. Ramaswamy, and B. Baldwin, *Textile Res. J.*, **66**(10), 651 (1996).
8. G. N. Ramaswamy, L. G. Ruff, and C. R. Boyd, *International Kenaf Conference*, Fresno, California, 138 (1993).
9. G. N. Ramaswamy, L. G. Ruff, and C. R. Boyd, *Textile Res. J.*, **64**(5), 305 (1994).
10. M. R. Vignon, D. Dupeyre, and C. Garcia-Jaldon, *Bioresource Technology*, **58**, 203 (1996).
11. K. M. Nebel, *Journal of the International Hemp Association*, **2**(1), 6 (1995).
12. C. Tofani and B. Ceschi, *Proceedings of the International Conference-Bast Fibrous Plants on the Turn of Second and Third Millennium*, Shenyang, China (2001).
13. M. Di Candilo, P. Ranalli, C. Bozzi, B. Focher, and G. Mastromei, *Industrial Crops and Products*, **11**, 197 (2000).
14. D. E. Akin, W. H. Morrison III, G. R. Gamble, L. L. Rigsby, G. Henriksson, and K. L. Eriksson, *Textile Res. J.*, **67**(4), 279 (1997).
15. G. Henriksson, *Textile Res. J.*, **67**(11), 829 (1997).
16. J. Dorada, B. Almendros, J. Field, and R. Alvarez, *Enzyme and Microbial Technology*, **28**, 550 (2001).
17. P. C. Das Gupta, K. Sen, and S. K. Sen, *Cellulose Chemical Technology*, **10**, 285 (1976).
18. M. A. Abd Alla, M. El-Sakhawy, and S. M. Kamel, *Polym. Degrad. Stab.*, **60**, 247 (1998).