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An empirical evaluation of structure–property relationships in natural fibres and their fracture behaviour

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An attempt is made in this paper to arrive at an empirical relationship between the structure and properties of lignocellulosic fibres through computer analysis. Significant regression equations for ultimate tensile strength (UTS) and percentage elongation of these fibres with structural parameters such as chemical composition, microfibril angle etc., have been arrived at using best fit. The results clearly indicate a narrowing down of the deviations between the observed and derived values of mechanical parameters reported earlier. This is attributed to (a) consideration of several structural parameters in the regression equation and (b) the analysis being free from any assumptions. Finally the fracture modes observed in these fibres have been classified and this is explained in terms of structure–property relationships.

1. Introduction

Natural fibres, one of the renewable resources, are extracted from different plants in large quantities mainly in developing countries. In addition to internal consumption in the countries of the origin, these fibres are exported to developed countries in various forms such as yarn, mats, mattings, brushes and fancy articles. However, in recent years there has been increasing competition for these fibres in many of their applications by synthetic fibres. This has resulted in under utilization of these fibres. It therefore becomes evident that attempts should be made to find new openings for this important natural resource. This calls for basic understanding of their structure properties and fracture behaviour.

1.1. Earlier work

Studies carried out so far on various natural fibres such as jute, coir, banana, sisal, sunhemp etc., have revealed the following:

Cellulose and lignin are the major chemical constituents of all natural fibres. These fibres are multicellular with minor changes in the arrangement of cells, their size and shape as revealed by optical and scanning electron microscopy. X-ray diffraction studies of the fibres have thrown light on the crystallinity and preferred orientation of the cellulosic matter in these fibres. The cellulose in the secondary walls of the cells of the fibres form by helical spirals of crystallites making a certain angle with the fibre axis [1]. This is termed as "microfibrillar or helical angle". The X-ray studies of the fibres have shown that the cellulose content of the fibres has cellulose I structure giving a characteristic X-ray peaks around *d*-0.386, 0.533 and 0.597 nm [2]. The properties of many of these fibres have also been reported from time to time [3–14]. Observed values of strength (UTS), modulus and percentage elongation of natural fibres are explained in terms of cellulose content and the microfibrillar angle with an early attempt as early as 1930. The crystalline cellulose has been found to be mainly responsible for the strength of the fibres. Various models have been proposed from time to time to explain the observed mechanical properties in these lignocellulosic fibres in terms of structural parameters. However, in most of these cases, a large gap between the observed and calculated values of the properties was observed thus indicating the simplicity of the assumptions made in those models. Stout and Jenkins [5] carried out systematic studies on a number of cellulosic fibres but did not use statistical analysis to estimate the extent of correlations and significance level. A large scatter in the properties was observed (Fig. 1). On the other hand, McLaughlin and Tait [9] were the first to carry out a detailed statistical analysis of structure–property relations and arrived at significant regression equations. In their analysis, the strength properties of various natural fibres were correlated with their helical angle and cellulose content. They have shown that modulus and UTS are not independent parameters but they can be correlated with a high level of significance. The regression equations derived by them for elongation and UTS show considerable deviation with correlation coefficient of 0.63 and 0.89, respectively, and actual data points show considerable scatter in comparison with calculated values from the derived equation (Figs 2 and 3).

1.2. Present work

From the foregoing it becomes evident that probably due to simplicity of models used for structurally complicated cellulose fibres along with the non-consideration of the effect of other structural parameters such as number of cells, their dimensions, defects in the fibre etc., a large scatter exists between

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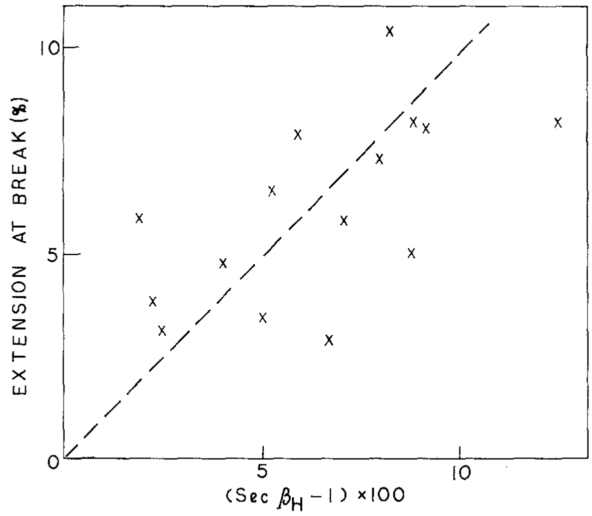

Figure 1 Relation between spiral angle and extension for leaf fibres (β_H is root mean square angle, Stout and Jenkins [4]).

the observed and calculated properties of natural fibres. Hence in this paper an attempt is made to overcome this by considering various structural parameters and their functions, which were not considered earlier, to correlate with observed properties using computer analysis to arrive at most significant regression equations for the structure–property relations. The method followed involves statistically determining the significance of the different structural parameters on the properties. Further an attempt is also made to explain the fracture behaviour of different fibres observed through scanning electron microscopic studies in terms of structural parameters.

2. Method of analysis

In this study fifteen fibres belonging to different kinds: bast, leaf and fruit fibres have been considered. Major chemical constituents, mechanical properties, number of cells, ultimate cell dimensions, helical angle etc., as reported by Stout and Jenkins [5] and mainly from the work carried out so far in this laboratory [10–14] have been taken into account for the analysis. The mean value of a population is taken as representative of any fibre parameter. Though there exists scatter in both structural parameters and properties, the mean value is likely to be a good approximation since all the parameters of a fibre have been derived from the same population. Also in a number of cases a large number of fibres were tested to arrive at statistically meaningful results. Various parameters of different natural fibres and their functions considered here are shown in Table I. Only UTS and percentage elongation are considered in the present study since modulus values are shown to be correlated with UTS [9].

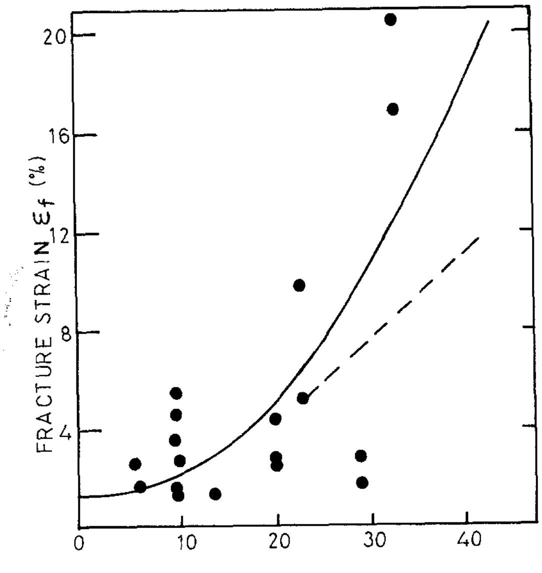

Figure 2 Mean fracture strains plotted against average microfibril angle on which a parabolic regression curve giving a correlation coefficient of $r = 0.691$ between predicted and measured results is superimposed [9]. (– – –) empirical trend for cotton after Rebenfeld; (——) regression curve (McLaughlin and Tait [9]).

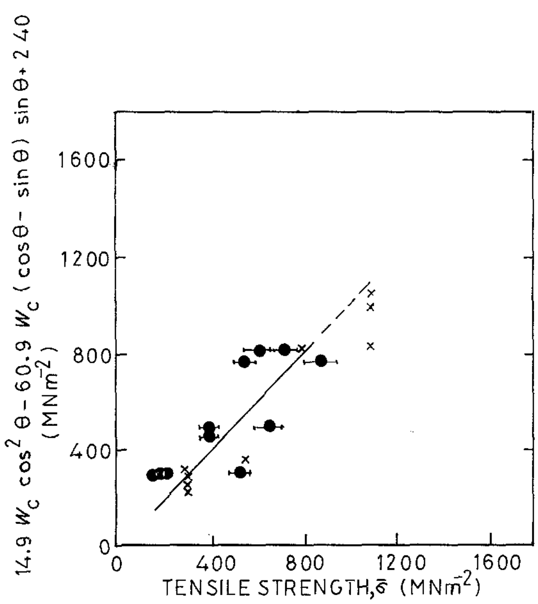

Figure 3 Calculated values from the predicted equation against observed mean values of predictions from the empirical equation plotted against mean tensile strength for various species of natural fibres [9]. (●) observed by the authors; (x) deduced from literature. $r = 0.80$ to 0.90.

Parameters such as shape and arrangement of cells (Fig. 4) were also considered in addition to three main structural parameters: cellulose content, microfibrillar angle and cell dimension for each kind of fibres (i.e. bast, leaf or fruit fibres) for deriving regression equations for UTS and % elongation to understand the extent of their correlation. But it was found that shape and arrangement of cells did not show any significant changes in properties. Hence further analysis was carried out using only three main structural parameters. Let "Y" denote the value of a physical parameter (e.g. UTS or percentage elongation) of a fibre which may depend on its structural parameters X_1 (cellulose content) X_2 (microfibrillar angle) and X_3 (cells dimensions).

We assume an empirical relation of the type

$$Y \propto X_1^{a} X_2^{a_2} X_3^{a_3} \qquad (1)$$

Where a_1, a_2 and a_3 can take any suitable value for the relation to hold good.

We get

$$Y_{\mathrm{th}} = K X_1^{a_1} X_2^{a_1} X_3^{a_3} + C \qquad (2)$$

Where K and C are constants for an equation. We then equate Y_{th} with the observed values for the specific

TABLE I Structure and strength parameters of various natural fibres [5, 10–15]

Fibres	Cellulose content (fraction) X_c	Spiral angle (θ)	Sin θ	Cos θ	Area of cross-section, $A \times 10^{-2}$ (mm^{-2})	Cell length, L (mm)	Cell length, to cell diameter (L/D) ratio	UTS (MN m^{-2})	% Elongation
1. Sisal	0.67	20.0	0.364	0.939	1.10	2.20	100	580	4.3
2. Pineapple	0.82	15.0	0.268	0.966	0.26	4.50	450	650	2.4
3. Banana	0.65	12.0	0.213	0.978	0.39	3.30	150	540	3.0
4. Coir	0.43	45.0	1.000	0.707	1.20	0.75	35	140	15.0
5. Ramie	0.83	7.5	0.132	0.991	0.03	154.00	3500	870	1.2
6. Hemp	0.78	6.2	0.139	0.994	0.06	23.00	906	690	1.6
7. Jute	0.61	8.0	0.140	0.990	0.12	2.30	110	550	1.5
8. Flex	0.71	10.0	0.176	0.985	0.12	20.00	1687	780	2.4
9. Sunn Hemp	0.69	9.5	0.167	0.986	0.71	8.00	284	440	5.5
10. Sansevieria	0.75	22.0	0.404	0.927	0.48	2.00	166	584	4.0
11. Maur hemp	0.64	22.5	0.414	0.924	0.66	1.90	142	500	5.2
12. Pita floja	0.72	20.0	0.364	0.939	0.44	1.75	145	600	3.6
13. M. Ensete	0.73	12.0	0.212	0.978	0.29	4.30	138	550	3.8
14. Talipot	0.50	24.5	0.456	0.910	0.40	1.15	47	210	3.1
15. Palmyrah	0.40	42.5	0.916	0.737	1.60	1.30	43	190	11.0

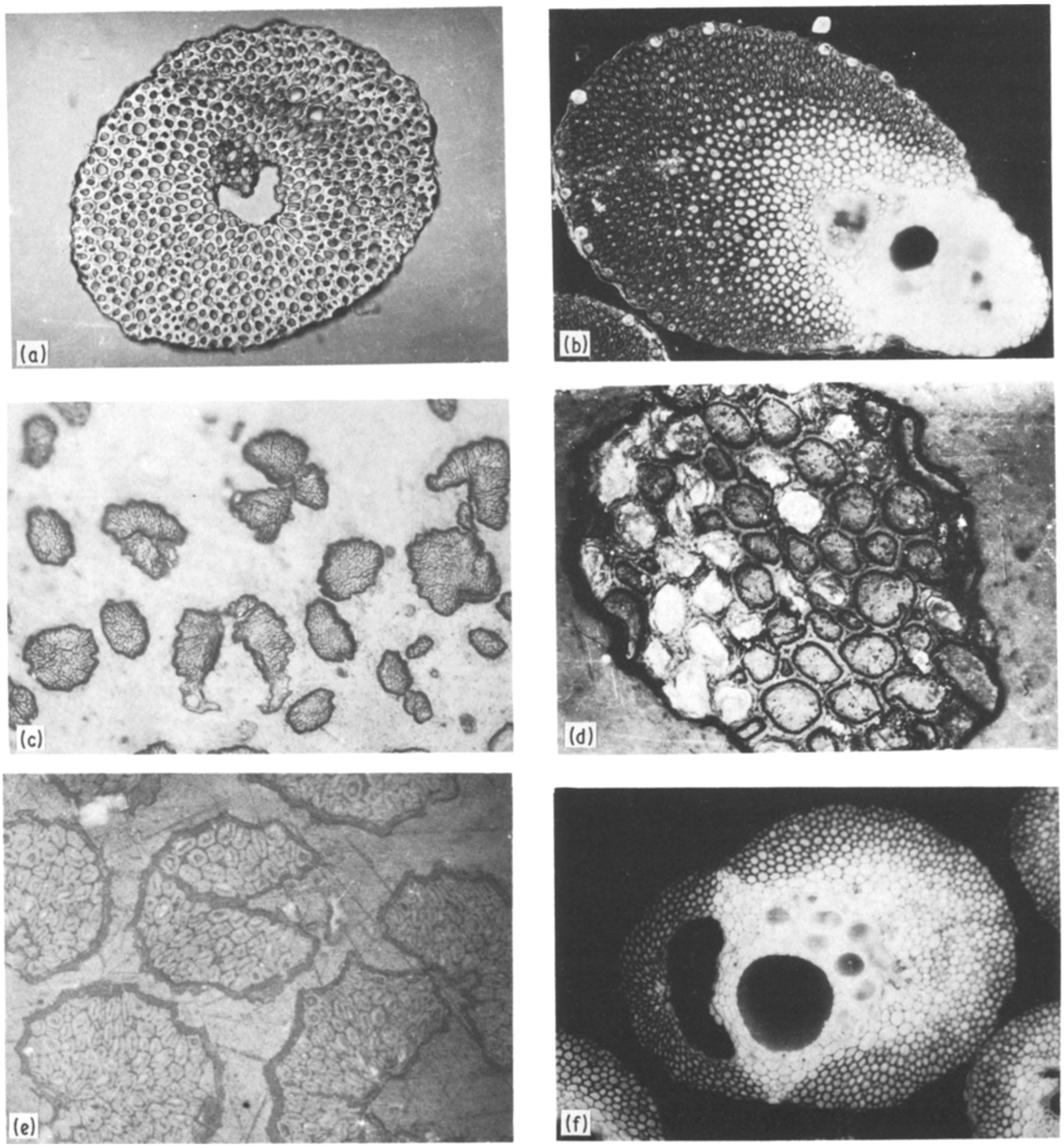

Figure 4 Optical micrographs of different cellulose fibres.

TABLE II Some of the computed results for empirical relation of tensile strength (σ)

Empirical equation used	Correlation coefficient	"t" value	"F" value
$X_C \cos^2\theta/(L/D)^{1/4}$	0.89	6.93	48.05
$X_C \cos^2\theta$	0.93	8.91	68.59
$X_C \cos\theta$	0.92	8.28	65.79
$X_C \cos\theta/(L/D)^{1/4}$	0.88	6.84	46.74
$X_C \cos\theta/(L/D)^{1/2}$	0.78	4.54	20.67
$X_C \cos\theta/A^{1/2}$	0.64	3.24	10.52
$X_C \tan'\theta$	0.52	2.36	5.59
$X_C \tan'\theta$	0.42	1.80	3.26
$X_C \cos\theta A^{1/2}$	0.64	3.27	10.68
$X_C A^{1/2}\tan\theta$	0.55	2.58	6.67

property parameter and put Equation 2 as

$$Y_{\text{th}} \simeq Y_{\text{obs}} = KX_1^{a_1}X_2^{a_2}X_3^{a_3} + C \qquad (3)$$

Inserting the respective values from Table I in Equation 3, we get fifteen equations for the fifteen fibres corresponding to a specific property of the fibres and a set of a_1, a_2 and a_3 values. Solving these equations we get the best fit values of K and C. The fitness of the equation thus arrived at is judged from the correlation coefficient and significance of the equation. By taking different values for the parameters a_1, a_2 and a_3, we arrive at different correlation coefficient and significance values. The best fit equation giving highest correlation coefficient and significance is chosen for the desired structure–property relation for the particular property of cellulose fibres. Variation in correlation coefficient with and without any one parameter indicates dependence or otherwise of this parameter on the observed property, i.e. an increase in correlation coefficient by introducing a structural parameter shows dependence of the parameter on the equation.

3. Results

It was found that in spite of using different types of relations for each type of fibre (bast, leaf or fruit), in the final analysis a single equation can be used for all the fibres. The computed results of the regressional analysis for different equations used for UTS are shown in Table II. Values of "F" and "t" determine the significance of the equations and correlation coefficient, respectively. Tables III and IV show some of the possible regression equations derived for UTS and % elongation, respectively, which are found to be highly significant. The two most significant equations for UTS and % elongation are given and these are plotted in Figs 5 and 6, respectively, which show the observed values against calculated values from the proposed equations. This may be compared with the Figs 1 to 3 obtained by earlier workers.

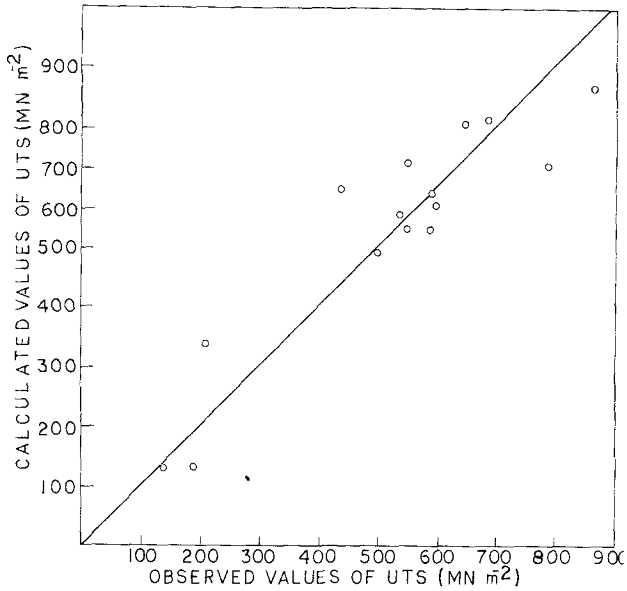

Figure 5 Calculated values from the derived regression equation against observed mean values of UTS of different natural fibres. Regression equation, $\sigma = 1050.1X_c\cos^2\theta - 97.50$. Correlation coefficient $\gamma = +0.93$.

4. Discussion

4.1. Structure–property relations

From the above analysis it is observed that cellulose content (X_c) and microfibrillar angle (θ) and cell dimensions (length (L)/diameter (D)) are likely to be the three most important parameters contributing towards the mechanical properties of cellulose fibres. The scatter between the observed values over the calculated ones for % elongation of different cellulose fibres, as shown in Fig. 6, clearly indicates the improvement of the present analysis over the earlier ones as shown in Figs 1 and 2. The scatter values are narrowed down with a correlation coefficient of 0.93 having a significance of 99.99% for the derived regression equation. The reason for this may probably be due to the consideration of the combined effect of the different structural parameters rather than considering one or two parameters (i.e. cellulose content and microfibrillar angle) as was done earlier [4, 9]. From Table IV, Equations 1 and 4 show that the introduction of the parameter L/D does not reduce the correlation coefficient but marginally improves the significance levels as evident by a small increase in the value of "F" and "t". This indicates dependence of these parameters (L/D) on percentage elongation. Hence this parameter should be included in the regression equation for elongation. Similarly, the best fit regession equation for

TABLE III Computer results of the most significant equations arrived at for the structure–property relations in cellulose fibre ultimate tensile strength (σ)

Regression equation	Correlation coefficent	"t" value	"F" value
$\sigma = 1197.8X_C\cos\theta' - 223.21$	0.92	8.28	65.79
$\sigma = 1050.1X_C\cos^2\theta - 97.50$	0.93	8.91	68.59
$\sigma = 123.0X_C\cos\theta(L/D)^{1/4} + 200.10$	0.88	6.84	46.74
$s = 120.5X_C\cos^2\theta(L/D)^{1/4} + 219.18$	0.89	6.93	48.05

TABLE IV % elongation (ε)

Regression equation	Correlation coefficient	"t" value	"F" value
$\varepsilon = 4.93 \dfrac{\tan \theta}{X_C} + 1.31$	0.93	08.91	79.40
$\varepsilon = 4.87 \dfrac{1}{X_C} - 4.07$	0.89	6.99	48.92
$\varepsilon = 9.09 \dfrac{1}{X_C \cos \theta(L/D)} 1/4 - 0.29$	0.88	6.68	44.58
$\varepsilon = 11.68 \dfrac{\tan \theta}{X_C(L/D)^{1/4}} 1.92$	0.93	8.94	80.68

UTS is found to have a correlation coefficient of 0.93 with a significance of 99.99% for the derived equation (Fig. 5).

However, the other parameters: defects in cellulose fibres which also have an important role in controlling the mechanical properties has not been considered in the present analysis. This is because of the availability of very limited data of quantitative estimation of defects in these fibres [12, 13]. If this parameter is also included in the regression equation, it is expected that the extent of correlation may still be improved upon and thus reduce the scatter values.

4.2. Fracture modes

From an observation of fractographs of the cellulose fibres studied so far (Fig. 7a to f), it is possible to classify the fracture modes in these fibres into two groups: (a) intercellular and (b) intracellular. Intercellular fracture may be defined as one in which propagation of crack is mainly between the cells, through the weak bonding material between the cells and hence pull out of the microfibrils is not generally observed. Such a fracture (Fig. 7a and b) is observed in fibres having lower elongation (< 4%) and are comparatively stronger. On the other hand, in the intracellular fracture (Figs 7c and d) the crack propagates through the cells and hence considerable pull out of the microfibrills is likely to occur. Such fibres are able to elongate more (> 4%) and are lower in strength. Intercellular fracture is found to occur in low elongation and high strength fibres and hence from Tables III and IV (showing the structure–property correlation), it can safely be concluded that such a mode of fracture is characteristic of cellulose fibres having high cellulose content, low helical angle and large L/D ratios. Similarly it can also be concluded that intracellular mode of fracture can be observed in the fibres having low cellulose content, high helical angle and small L/D ratios. However, there can be a mixed mode of fracture in some fibres depending on the variation in the above structural parameters. Sisal fibre (Fig. 7e) is found to have such a mixed mode of fracture.

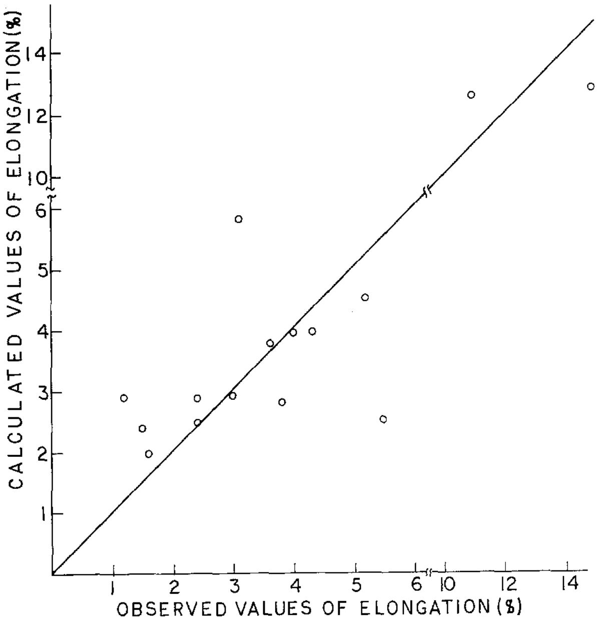

Figure 6 Calculated values from the derived regression equation against observed values of elongation of different natural fibres. Regression equation, $\varepsilon = 11.68[\tan \theta/X_c(l/d)^{1/4}] + 1.92$. Correlation coefficient $v = +0.93$.

However, the fracture mode may also be dictated by the defect parameter, importance of which has been mentioned earlier. Presence of considerable defects reduces the elongation and thus lead to intercellular fracture irrespective of other structural parameters. This is clear from Fig. 7f which shows the fracture tip of a talipot fibre which in spite of having lower cellulose content and higher microfibrillar angle show intercellular fracture because of the presence of a considerable number of defects present in the form of lacuna in addition to thin cell walls as is evident from Fig. 7f. The present study thus clearly brings out the necessity of a systematic study of structure–property relation in cellulose fibres by considering various structural parameters rather than considering only one or two parameters. Such a study may help in deriving research imperatives for better uses of these fibres which may include improvement of fibres properties, incorporation of the fibres in polymers/cement matrices to fabricate composites. In fact there have been already some attempts made in this direction [15–20].

5. Conclusions

(i) A regression equation has been arrived at using computer analysis correlating observed properties (UTS and % elongation) and structural parameters of natural fibres irrespective of their origin: bast, leaf or fruit. Such a correlation will help not only in understanding the behaviour of the fibres under tension but also in predicting the properties of other natural fibres.

(ii) It is found that in addition to cellulose content and microfibrillar angle, other structural parameters such as cell dimensions, defects etc., should be

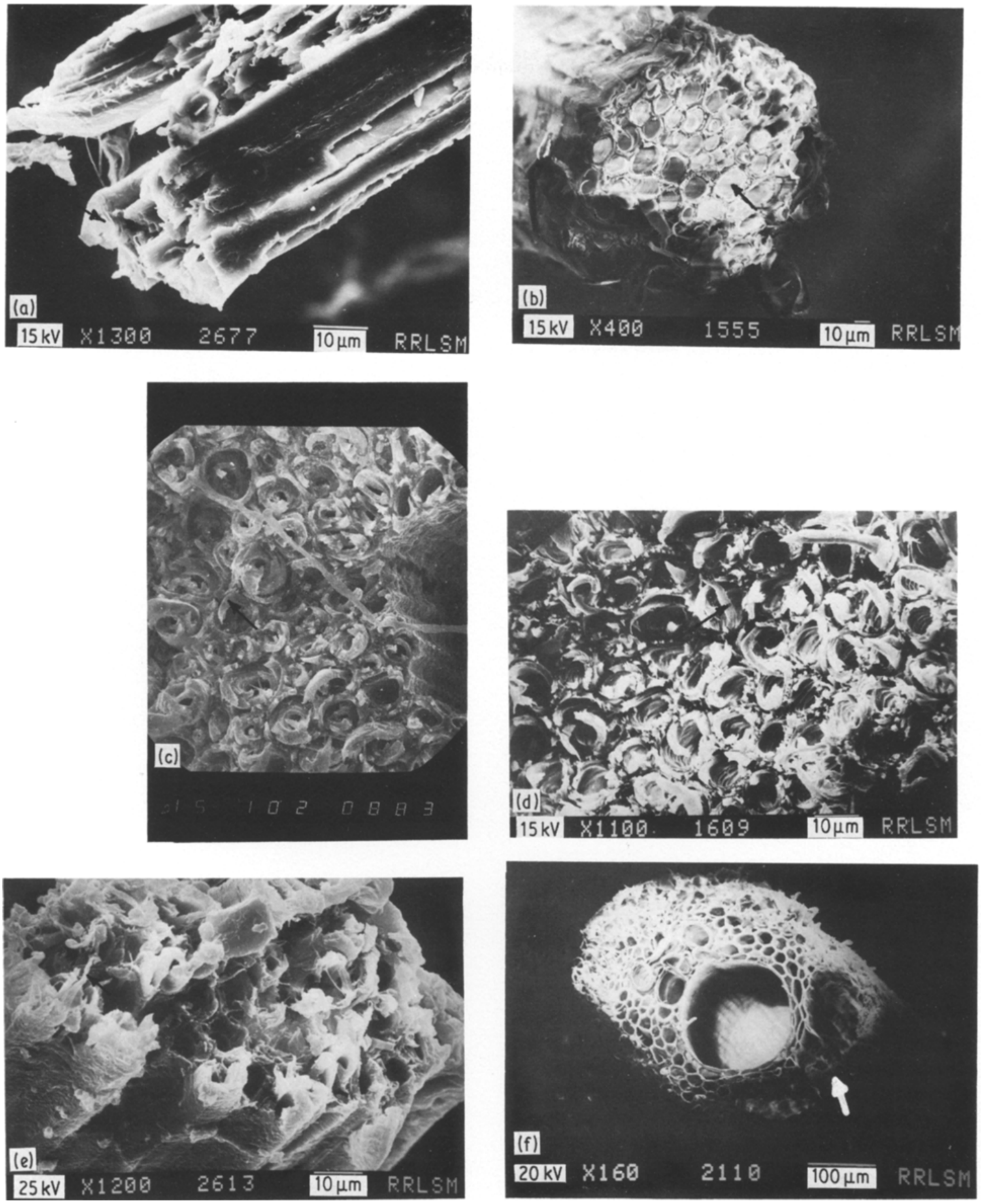

Figure 7 SEM photographs of the fractured tips of different cellulose fibres showing (a) and (b) intercellular fracture showing absence of pullouts of microfibrils, (c) and (d) intracellular fracture showing presence of considerable pullouts of microfibrils, (e) mixed mode of fracture showing occasional pullouts of microfibrils, (f) intercellular fracture due to defects.

considered in deriving relations between structure and properties.

(iii) By the incorporation of cell dimensions into the equation, a correlation of 0.9 at significance of 99.99% has been arrived at for % elongation and UTS values thus bringing down the scatter between observed and calculated values to a minimum.

(iv) The fracture modes observed in the natural fibres have been clearly understood in terms of structure–property correlations. The fracture mode is classified depending on this correlation.

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