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The Chemical Nature of Ramie *(Boehmeria Nivea (L) Gaud)* Fibre

KEYWORDS Ramie fibre, Gum, Chemical degumming, α-cellulose, Tensile property.

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ABSTRACT *Ramie (Boehmeria nivea L.Gaud), a nettle family, is derived from the bark of the stem. Bast fibres are obtained from the stems of various plants but ramie differs in many important characteristics. Ramie fibre obtained contains a high proportion of gummy polysaccharides, whose removal is necessary for further processing. The main portion of the gum has been found to be of the nature of glucan, a polysaccharide. On extraction of the gum, the fibre bundles break up into ultimate fibres having a fibrillar structure. Quantitative analysis of chemical constituents and fibre characteristics have been studied by using standard methods of R 67-34 Variety. It is observed that progressive removal of residual gum increases the α-cellulose content with a trace of lignin. The IR spectrum of degummed and bleached ramie reveals the successful removal of gums and it is similar to that of pure cellulose, indicating about 94% alpha-cellulose.*

INTRODUCTION

Ramie (*Boehmeria nivea L Gaud*), a member of the urticanceae or nettle family, is one of the oldest vegetable fibre which is derived from the bark of the stem. Bast fibres are traditional fibres obtained from the stems of various plants but ramie differs from bast fibre crops in many important characteristics. Firstly, ramie plant is very hardy perennial, shrubby in habit which under suitable conditions can be harvested 4-5 times a year. Secondly, unlike jute and flax which is obtained by retting the stem in water, the ramie fibre is extracted from the green stalk mechanically by decortication, washing known as raw ramie ribbons (r.r.r.).

Its popularity in the textile industry is limited because degumming plays a major constraint for its commercial use in world trade. Though ramie and cotton are unicellular fibre, chemically both are highly cellulosic with a trace of lignin whereas jute, a multicellular fibre consists a fairly high amount of hemicellulose and lignin[1]. It is considered as a valuable textile material for its high strength especially wet strength, lustre and microbial resistivity which make it unique in the textile world. However, various methods on chemical [2-8], microbial[9-12]and enzymatic degumming[13-14] have been reported in the literature but reports on efficient degumming and bleaching been covered under Patents[15-19]give very scanty information about methods adopted for degumming vis-à-vis the properties of the fibre thus obtained. Little work has been reported on the chemical analysis of ramie fibre at different residual gum contents.

Dasgupta et al[2] is of the opinion that the use of sodium hydroxide at high temperature has been found to be the most effective agent for degumming decorticated ramie fibre. Allison[6] advocated a milder open cooking system which brings about a loss of 10-12% on the weight of the fibre. Chakraborty[20] et al suggested that as the ramie fibre was progressively degummed to about 2% residual gum content, the fineness, tenacity especially the wet strength of the fibre improved, the fibre become more extensible, absorbed less moisture, dried out at a quicker rate, separated into individual cells and the fibre to fibre friction became lower. Kundu et al[21-22] reported that chemical degumming treatments on decorticated ramie fibre have been found to be satisfactory with a reduction in tenacity of degummed fibre compared to control. Thakur et al[23] reported the chemical composition and fibre characteristics of raw and degummed ramie of three different varieties opined that the loss in tenacity on degumming may be attributed to the removal of binding material in the cells. Since the fibre is multicellular, the removal of hemicellulose or the cementing substances would, in turn, be reflected in lower tenacity over control fibre irrespective of varieties.

Ramie has diverse applications though it has not been exploited for commercial uses. The use of natural fibre due to the increasing ecological consciousness cannot substitute for traditional cellulosic fibre which are expensive but also help to boost the national economy. The present work is aimed to provide basic information on quantitative analysis of chemical constituents and fibre characteristics by using standard methods of indigenous R 67-34 Variety and reported.

EXPERIMENTAL PROCEDURE

Materials

Decorticated ramie fibre (R 67-34 variety) was received from the Ramie Research Station, Central Research Institute for Jute and Allied Fibres, Sorbhog, Assam. All chemicals were analytical grade. Chemical degumming of decorticated ramie fibres were carried out to different residual gum content following a simple degumming method by Dey[24] in ROACHES Dyeing Machine. Samples with different gum contents were prepared by treating decorticated ramie fibre with 1% hydrochloric acid and treatment with 0.5-2.0% sodium hydroxide solutions at 100°C for 1 hr. Bleaching of degummed ramie fibre at different alkali concentration are also carried out. Ten samples with different residual gum content ranging from 22.72- 3.79 were examined.

Methods

Ramie (decorticated or defatted as the case may be) was

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cut into small pieces and then used. The chemical constituents of decorticated and treated ramie samples were determined by standard procedures[25]. Each of the estimation was performed in duplicate and the average value was recorded; the results are given in Table 1.

Estimation of Gum content: [1]
Decorticated ramie fibre was combed to remove any adhering bark and then cut to small pieces. A weighed fibre sample was then subjected to the following successive treatments and the solution after each treatment was filtered through a weighed sintered glass crucible:

Treatment with 0.3% hydrochloric acid at room temperature for 0.5 hr. with material to liquor ratio of 1:50 and washed free of acid with water.

Treatment with 1% sodium hydroxide solution (liq. ratio, 1:100) at 94°-96°C (bath temperature) for 1 hr.

Repeated the treatment (ii).

Treatment with 5% sodium hydroxide solution (liq. ratio, 1:100) at 94°-96°C (bath temperature) for 1 hr.

Finally the sample was washed, soured with1% acetic acid, washed thoroughly with hot water, dried at 105°C and weighed. The loss in weight or the gum content was calculated on the dry weight of the decorticated fibre.

It was observed that more uniform results were obtained by removing the gum in stages. For the extraction of resistant polysaccharides, 4-5% alkali at 95°C was used.[26]

Measurement of linear density:
Linear density (Weight in gram of 1000 m long fibre weight) of fibres was measured by gravimetric method. 100 fibres each of 1 cm cut length were taken and weighed from 2 lots and the mean weight of the two lots in mg will give the gravimetric fineness in tex.

Determination of bundle tenacity:
Bundle tenacity was determined by J.T.R.L Fibre Bundle Strength Tester by taking a bundle of fibres (250-300mg) of 12.5 cm length.[27]

Susceptibility of ramie to microbial damage:
The soil burial test is the universal method of testing rot resistance and is most suitable for testing goods treated with antiseptics. Samples of ramie with different gum contents were combed to remove barky and entangled fibres and then cut to about 15cms length from the middle portion. Rot resistance of ramie fibres is assessed by subjecting the fibres to a standard soil burial test for 21days at 30 ± 2° C in an incubator. After the specified period of soil-burial, the fibres are washed successively with water, detergent solution, water and alcohol before drying them under vacuum at 50°C. Bundle tenacity was determined by J.T.R.L Fibre Bundle Strength Tester. Rot resistance is expressed as a (%) of strength retained after soil burial under the specified condition. The test soil is prepared by mixing thoroughly fertile garden soil, cowdung and sand in the proportion of 2:1:1, sieving the mixture and adjusting the moisture content of the compost to 25-27°C.[28]

Evaluation of Surface appearance property:
Whiteness index in the "HUNTER" scale, yellowness index in the "ASTM D1925" scale and brightness index in the "TAPPI 45"scale of decorticated and degummed ramie fibres were measured by the Spectrascan-5100® computer colour matching system using relevant softwares. Spectrascan-5100® computer colour matching system was used to measure the surface colour strength properties of fibres, viz., K/S Value at the maximum absorbance wavelength (λ_{max}, at 350nm) using relevant softwares.

Infrared Spectrophotometry:
Finely cut ramie fibres (2mg) were examined by a Shimadzu double beam model 440 spectrophotometer from 4000-500 cm^{-1} under a normal slit program and a scanning speed of nearly 19s/100 cm^{-1}. A KBr pellet without the sample was used in the reference beam.

RESULTS AND DISCUSSION
The ten fibres chosen in the present investigation show considerable difference in chemical constituents on degumming and bleaching. The chemical constituents of ramie fibre of varying gum content are shown in Table 1 whereas the comparative studies of ramie fibre with cotton, a unicellular fibre and jute, a multicellular fibre are shown in Table 2.

The fibre properties and their response to chemical treatments depend to a large extent on the chemical composition of the fibre. It is well known that cellulose forms the major portion of all vegetable fibres. The results in Table 1 indicate the different constituents of ramie at different stages such as decortication, degumming and bleaching. It reveals that decorticated ramie contains high α-cellulose and hemicellulose with a low lignin content. The non-cellulosic constituents not only act as cementing materials of the ultimate fibre cells but form an essential part of the fibre structure. Removal of non-cellulosic constituents chemically leads in disintegration of fibre. Lignin and hemicellulose have a structural function similar to that of cellulose forming together with the latter, the skeleton of the fibre. These components are believed to contribute to mechanical strength of fibre.

It is noticed that during degumming, sodium hydroxide affects both hemicellulose and lignin which is sufficient enough to remove the encrusting gummy material. It is clear that during degumming, the progressive removal of hemicellulose is noticed with varying concentration of sodium hydroxide solution (0.5 to 2.0%) for 1 hr. at 100°C. The fibre becomes finer as a result of removal of hemicellulose, lignin and probably other substances. The colour of the fibre also changes from light brown to creamy in colour.

TABLE 1: Chemical Constituents of Ramie Fibre

Constituents	Material									
	Decorticated Ramie	Decorticated and Bleached Ramie	Degummed Ramie at different Alkali Concentration				Bleached Ramie Fibre			
			0.5	1.0	1.5	2.0	0.5	1.0	1.5	2.0
α-Cellulose	81.10	84.50	89.10	90.30	90.80	91.70	93.30	94.10	94.30	94.50
Hemicellulose	13.40	11.30	8.90	8.20	7.80	7.00	3.80	3.30	3.10	2.90
Lignin	1.40	0.90	0.80	0.60	0.50	0.40	0.50	0.40	0.30	0.20
Fat and Wax	0.40	0.30		0.30				0.20		
Ash	1.6	1.60		1.40				1.30		
Gum content	22.72	20.66	6.10	5.47	5.29	5.15	4.66	4.25	3.98	3.79

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TABLE 2: Comparative studies of Chemical Composition of Bast Fibres & Cotton

Material Properties	Ramie			Flax	Hemp	Jute	Cotton
	Decorticated	Degummed	Bleached				
α-cellulose	81.10	90.30	94.10	70.3	70.8	60.7	92.89
Hemi-cellulose	13.40	8.20	3.30	9.2	11.0	23.9	2.67
Lignin	1.40	0.60	0.40	5.5	5.0	12.5	0.54
Fat & Wax	0.40	0.30	0.20	2.6	1.9	1.0	0.85
Ash content	1.6	1.40	1.30	1.5	1.9	0.79	1.32
Pectin	1.82	0.62	0.41	1.8	-	1.60	0.58

TABLE 3: Comparative Studies of Ultimate Cell dimensions of Natural Fibres

Ultimate Cells	Ramie	Flax	Hemp	Jute	Cotton
Length(L)mm	20.0-250.0	25.0-65.0	5.0-50.0	0.8-6.0	15-60
Breadth(B)x10^{-3}mm	15-80	10-35	10-40	5-25	15-20
L/B ratio	3500	1700	900	110	1300

Removal of hemi cellulose and lignin during bleaching of the degummed ramie fibre gradually decreases as expected. In general, bleaching holds the key for successful removal of the colouring matter present in the fibre. For pure white fibres, bleaching is essential resulting a marginal loss in weight and strength. Hydrogen peroxide, a bleaching agent was used because it has mild delignification effect and the fibre retain adequate strength. It also helps in better cleaning and separation of ultimates, thereby improving the fibre quality. Bleaching of degummed material with 0.5% sodium hydroxide results higher loss of hemicellulose content. It may be attributed to the alkali added in the bleaching bath which simultaneously reacts with the non-cellulosic matter present even after degummed material with 2% sodium hydroxide, due to the less non-cellulosic matter present in the degummed material. A similar trend is observed in case of degummed material 1.0% and 1.5% with alkali concentration. The non-ionic surfactant used during bleaching enhances the bleaching effect of hydrogen peroxide on fibre.

Another noticeable change is that the fibre becomes finer as a result of removal of hemicellulose and other substances. Degumming with 1% alkali concentration, the hemicellulose content is reduced to 25% and lignin content to about 29% compared to decorticated ramie fibre. It can be concluded that 1% alkali causes degumming and swelling of the fibre which makes the fibre to separate from the cementing matrix.

The combined degumming and bleaching of decorticated ramie fibre does not give satisfactory result. The reason may be due to the presence of insufficient alkali which are unable to remove hemicellulose, lignin and probably other substances from the cementing matrix as well as the required temperature needed to remove the incrusting gummy material. The hemicellulose content in the decorticated/bleached ramie fibre is reduced to 84% whereas lignin to 64% compared to decorticated ramie fibre.

It is clear from Table.4 that the fineness and bundle strength of degummed ramie fibre improved remarkably by 44 % in Fineness and 26.80% approximately in bundle tenacity over decorticated ramie fibre. The improvement in fineness of the degummed ramie fibre may be ascribed due to the removal of the adhering gum. Removal of the adhering gum enables the fibre to take a more crystalline form resulting in increase in bundle tenacity. The improvement in fibre fineness and bundle tenacity of decorticated/bleached ramie fibre is not significant because the degumming process is poor. It is well known that progressive degumming leads to gradual increase in tenacity of fibre. If it is assumed that the gummy matter contributes little to the tensile strength of ramie, then bundles of equal length and weight would contain more and more of the fibre substance to break as the gum is progressively removed. This may explain the gradual increase in tenacity with decreasing gum content. The colour strength value (K/S) goes on decreasing and this indicates that the fibre become whiter. The whiteness and brightness indices of ramie fibre increase on degumming and improve further on bleaching.

Decorticated ramie having any gum content can be degummed to any desired residual gum content with varying alkali concentration, temperature and time of treatment. When decorticated ramie fibre samples were treated with 1% sodium hydroxide solution at 100°C, the residual gum content of the degummed fibre reduces to 5.47% with a 76.77 % of gum removal. The findings of Dasgupta et al reveals that addition of sodium sulphite to the extent of 0.5% improves the tenacity of fibre by reducing the degradative action of oxygen on cellulose in presence of hot alkali but improvement of tenacity in dry and wet condition can be achieved without the addition of sodium sulphite in this study, thereby reducing the cost of degumming.

The IR spectra of before and after degumming are shown in Fig 1. Ramie consists of α-cellulose, hemicellulose, lignin, gum and other components. Pectin is a heterogeneous group of acidic structural polysaccharides that have complex structure. After degumming, the residue is nearly pure ramie fibre. It is commonly recognized that ramie fibre consists of linear macromolecules formed by β-D-anhydroglucose units linked by 1,4-glucosidic bonds[29]. The spectrum of degummed ramie fibre exhibited O-H stretching absorption around 3420cm^{-1}, C-H stretching around 1645cm^{-1} and 2900-3000 cm^{-1} and C-O-C stretching around 1063cm^{-1} and 1105 cm^{-1}. These absorption bands are consistent with those of a typical cellulose backbone[30]. In the structure of ramie, there are many other non-cellulosic substances such as hemicellulose, pectin and lignin which contain chemical bonds such as O-H, C-O-C, C-H etc, thus the corresponding intensities in the spectrum of ramie are higher as compared with that of degummed fibre.

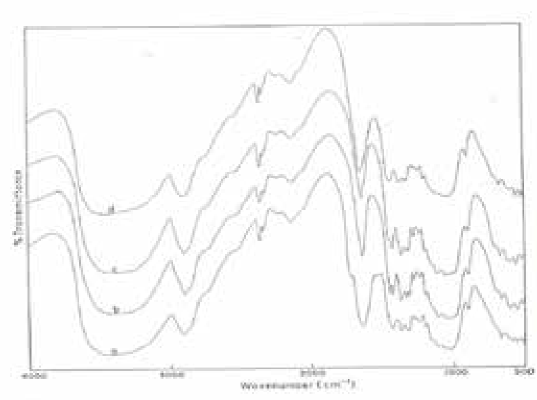

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Fig.1: INFRARED SPECTRA OF
a) Decorticated ramie fibre
b) Degummed ramie fibre
c) Degummed/bleached ramie fibre
d) Decorticated/bleached ramie fibre

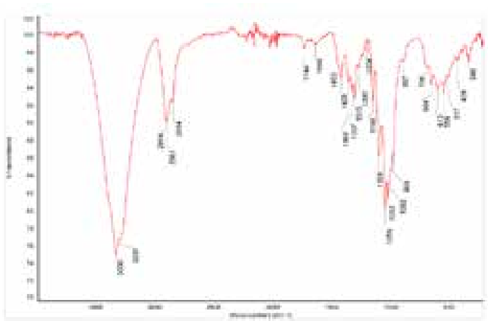

Fig.2: Infrared Spectra of cotton fibre

All the characteristic peaks representing gum in ramie are absent in Fig 1b. The peak at 1719 cm^{-1}, characteristic of the carbonyl group of uronic acid (a constituent of hemicellulose) is present in the spectrum of decorticated ramie. With the alkali treatment during degumming and bleaching, the intensity of the band is reduced or disappears. It is thus observed that in alkali treatment substantial portion of uronic acid, a constituent of hemicellulose xylan, is removed resulting in the disappearance /reduction in its intensity. Only those peaks characteristics of cellulose, viz. 3500-3000 cm^{-1}, 1375-1370 cm^{-1} and 1055 cm^{-1} are much prominent in the spectrum of processed ramie indicating that ramie fibre is chemically composed of pure cellulose. A trace of Infrared spectra of cotton fibre in given in Fig.2 for reference. IR spectral study thus clearly indicates the efficiency of degumming method. From the spectra of degummed fibre we can conclude that mainly non-cellulosic substances were removed from decorticated ramie.

The results of soil burial test of ramie fibres are shown in Fig3. It reveals that under soil incubation, the fibres are buried inside the soil compost and were in ultimate contact with a number and variety of microorganisms of soil and cowdung. In the buried condition, decorticated ramie reveals a poor retention of tensile strength of 10.82%. Upon chemical degumming, the retention of tensile strength is increased appreciably from 10.82% to 86.80%. A further bleaching of degummed fibre the retention reaches to 94.74%. α-cellulose of ramie is highly crystalline and as such microorganisms cannot grow directly on it. Gums of ramie fibre being a heterogeneous carbohydrate complex serves as a ready nutrient and source of energy to the damaging microbes. Thus it indicates that more the gum content of the fibre, more is the extent of damage. Degumming helps in increase of susceptibility to microbial damage with the removal of gum which is composed principally of hemicelluloses (arabans and xylans).

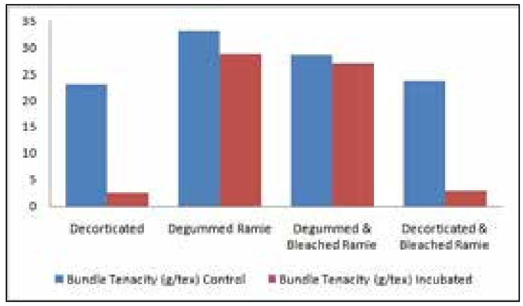

Fig.3: Bundle Strength of Ramie fibre before and after soil burial test

SUMMING UP, WE CAN CONCLUDE

The comparative data on the length and breadth of ultimate cells of various bast fibres indicate that the *L/B* ratio of ramie is superior to the other bast fibres and accordingly it is named as king of all natural fibre.

The *L/B* ratio also indicate its use as a source of cellulosic raw material in textile and non-textile applications. It could also be used in different phases of application such as canal lining, river bank restoration due to higher wet strength.

Degumming and bleaching of degummed ramie fibre shows improvement in alpha cellulose content with removal of gum. A significant decrease in lignin and removal of hemicellulose substantially upon progressive removal of gum can be achieved.

It was observed that degummed and bleached ramie fibre to gum content to 3-6% can be separated into individual filaments required for development of finer yarns either on short or long staple system. The microbial resistance of the fibres could not be achieved unless degummed below 5-6%.

So it is evident that decorticated ramie should be degummed to below 6% and preferably to 2% depending on the spinning system so that the characterization of the fibre e. g tenacity, fineness and microbial resistivity are fully realized. Allisons[6] partial degumming method with a yield of 90% may not produce the fibre of desirable quality.

TABLE 4: Comparative Fibre Characteristic Study of Ramie

Properties	Tenacity (gm/tex)		Elongation (%)		Fibre Fineness (Tex)	Whiteness Index (HUNTER)	Yellowness Index (ASTM 1925)	Brightness Index TAPPI 45	RFL At 440 nm	K/s Value at 360 nm
	Dry	Wet	Dry	Wet						
Decorticated Ramie	27.05 (16.85)*	29.60 (16.34)	2.66 (34.52)	2.05 (19.72)	1.39	61.21	42.69	30.43	27.87	0.54
Degummed Ramie	34.30 (10.17)	44.69 (19.34)	2.19 (32.82)	2.73 (24.28)	0.78	67.02	25.47	40.50	38.48	0.27
Bleached Ramie	28.86 (21.40)	35.66 (15.39)	1.33 (39.70)	3.67 (26.63)	0.63	85.76	10.24	70.54	67.96	0.04

Decorticated and Bleached Ramie	28.16 (16.21)	30.63 (15.85)	2.54 (30.58)	2.17 (20.62)	1.34	62.46	40.83	31.97	29.34	0.54

*** Figures in the parenthesis indicate C.V%.**

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