

Reeds-A Potential Source of Raw Material for Production of High Alpha-Cellulose Pulp

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ABSTRACT

High alpha-cellulose was extracted from two varieties of reeds, viz. Ekra (Erianthus longisetus) and Khagra (Neyraudia reynaudiana), by following water prehydrolysis sulphate process. Pre-hydrolysis was carried out at three different temperatures viz. 135, 145 and 155°C for 2.5 and 3h. Kraft cooking was done for all the batches of prehydrolyzed chips and the characteristics of unbleached pulp were evaluated. Selected batches of unbleached pulp were bleached using C-E-H-E-H-dil. HCL sequence under controlled conditions. Bleached pulps with brightness 85-88% were obtained, having alpha-cellulose 92.5-94.8%, pentosan 2.12-2.90% and ash 0.05-0.08%. Analytical data on raw material, prehydrolyzed chips, unbleached and bleached pulps were presented. The alpha-celluloses were further characterized with the help of IR, X-ray and thermal analyses.

INTRODUCTION

The conventional raw materials like soft wood, hard wood and bamboo used for pulp, paper and cellulose-based industries are depleting day by day and it is predicted that by the turn of the century, there will be a global shortage of these raw materials. During the last three decades though many of the forest based fast growing annual and perennial plants have been identified as alternative source of raw materials for pulp and paper making (1-6), but very little work has been done on the production of high alpha-cellulose pulp from such raw materials. The high alpha-cellulose or dissolving cellulose finds application in many chemical and paper making end uses and is principally used for manufacture of esters and ethers, lacquers, plastics, vulcanized fibre, artificial leathers, sponges and grafted products etc. (7-12). There is considerable variation in the compositional characteristics of plant materials from species to species. It is therefore, absolutely necessary to examine each and every variety individually for its suitability for the preparation of high alpha-cellulose pulp.

Ekra reed (Erianthus longisetus) and Khagra

reed (Neyraudia reynaudiana) grow wild on the banks of river Brahmaputra and in the forests of N.E. region of the country and are available in large quantities annually (13). The reeds are tall, tufted perennial grass with robust smooth stem and culms.

Considering the importance of non-wood fibres, systematic studies were carried out to evaluate the two reed species for preparation of high alpha-cellulose pulps. In this paper, data on laboratory scale preparations of the pulps and their characterization are presented.

EXPERIMENTAL

Raw material

For the present investigations reeds were collected from the bank of the river Brahmaputra, in the District of Jorhat, Assam, India. The reed culms were cut into 2.5cm in length and the chips were air dried and then used for the experimental works on oven dry (od) basis.

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Table-1			
Proximate Chemical Analysis			
Particulars		<i>E. longisetus</i>	<i>N. reynaudiana</i>
Solubility in:			
Cold water,	%	6.22	5.12
Hot water,	%	10.25	8.36
1% Alkali,	%	29.80	30.20
Alcohol benzene (1:2),	%	2.70	2.82
Lignin	%	19.23	20.70
Pentosan	%	20.35	19.42
Cross & Bevan cellulose	%	56.57	57.57
Ash	%	2.12	2.04

Proximate chemical analysis

The air dried chips were powdered in a Wiley mill and screened through -40 and +60 mesh wire. The portion remained in between the two screens was used for proximate chemical analysis adopting TAPPI standard methods (14). The results obtained are given in Table-1.

Prehydrolysis of chips

1000g of chips (as od matter) was cooked using deionized water at M:L ratio 1:5% in a 10 litre capacity stainless steel electrically heated rotary digester. The hydrolysis was carried out at different conditions (Table-2).

The time taken to raise the temperature to maximum was 90 min. After the cooking the prehydrolysed chips were first washed with tap water and then with distilled water and finally air dried.

Pulping of prehydrolysed chips

Cooking experiments were carried out using 500 mg (od) of prehydrolysed chips with 17% active alkali (NaOH+Na₂S) as Na₂O for 3h at 163±2°C at M:L ratio 1:5, maintaining sulphidity at 20%. After the cooking, the pulp was washed with fresh water and then with distilled water and finally air dried and analyzed. Pulping conditions and analytical data on unbleached pulp are given in Table-3.

Bleaching

The screened unbleached pulp from each cook was bleached by a typical multistage bleaching process, involving chlorination (C), alkali extraction (E), sodium hypochlorite treatment (H), alkali extraction (E) and sodium hypochlorite treatment (H) sequence. Finally, a mild HCl acid treatment was given to the

pulp for improving the brightness and to prevent colour reversion (7). This treatment also reduced the ash content of the bleached pulp to a certain extent. The conditins of bleaching are reported in Table-4.

Evaluation and characterization of bleached pulps

The yield of bleached pulp, pentosan, alpha, beta and gamma-celluloses, copper number, ash and brightness were determined as per Tappi standard methods (14). Degree of polymerization (DP) and carboxyl contents were determined as per methods suggested elsewhere (15,16). The results are given in Table-5.

Fibre morphology

Morphological characteristics of the unbleached fibres, taken from batch No.5 and 9, were determined by using a Dokuval photomicroscope (JEOL, Japan) at different magnifications. About 200 fibres of various sizes were measured for their length, diameter, cell wall thickness and the average values of the results are given in Table-6.

Infrared and X-ray diffraction

IR spectra of alpha-cellulose was recorded on a Perkin Elmer spectrometer (Model 2000-FTIR) using the KBr disk technique from 4000 to 450 cm⁻¹ with a resolution of 2 cm⁻¹ with five scans per sample. X-ray diffraction pattern were recorded using a computer controlled X-ray diffractometer (Type JDX-11 P3A, JEOL, Japan) with pulse height analyser and scintillation counter NaI (T1) single crystal.

Thermal behaviour

Thermogravimetry (TG) and differential thermogravimetry (DTG) were carried out using a Shimadzu Thermal Analyser 30. The mass of the

Table-2

Prehydrolysis conditions and analytical data of prehydrolysed chips

Particulars	Ekra reed			Khagra reed		
Prehydrolysis:						
Time, h	2.5	3	2.5	3	3	3
Temp, °C	135	145	135	145	135	145
Batch No.	1	2	3	4	5	6
pH of prehydrolysis liquor	4.1	3.9	3.7	4.0	3.8	3.5
Yield, %	84.7	82.9	81.2	83.0	81.0	79.9
Pentosan, %	16.2	14.0	11.8	15.7	13.1	10.9
Ratio of Pentosan removal, * %	35.57	42.97	52.92	35.97	47.86	57.20
Ratio of removed Pentosan to dissolved matters ** %	43.32	51.13	57.28	43.05	51.26	57.91
Lignin %	18.4	17.9	17.0	18.1	17.2	16.3
Ratio of lignin removal * %	18.96	22.83	28.22	21.88	27.55	32.27
Ratio of removed lignin to dissolved matters ** %	23.83	25.68	28.86	24.75	27.88	30.88
Alcohol benzene solubility %	3.3	3.9	4.4	3.4	4.0	4.7
* Ratio of pentosan/lignin removal	$= \frac{A-B \times \text{yield}}{A} \times 100$					
** Ratio of removed pentosan/lignin to dissolved matters	$= \frac{A-B \times \text{yield}}{100 - \text{yield}} \times 100$					

Where A : Pentosan/lignin in original raw material; B : Pentosan/lignin in prehydrolyzed material (15)

Table-3

Conditions of sulphate pulping and analysis of unbleached pulp

Particulars	Ekra reed						Khagra reed					
	2.5	3	135	145	155	155	2.5	3	135	145	155	155
Prehydrolysis:												
Time, h	2.5	3					2.5	3				
Temp, °C	135	145	135	145	155	155	135	145	135	145	155	155
Batch No.	1	2	3	4	5	6	7	8	9	10	11	12
Yield, * %	34.2	33.3	31.8	33.9	32.0	31.2	34.5	33.8	32.6	33.8	32.7	31.8
Pentosan, %	6.3	5.9	5.1	6.0	5.2	4.9	5.8	4.8	4.2	5.2	4.3	4.0
Ratio of Pentosan removal, %	89.41	90.35	92.03	90.01	91.82	92.49	89.70	91.65	92.95	90.95	92.76	93.45
Ratio of removed Pentosan to dissolved matters %	27.65	27.56	27.46	27.71	27.48	27.36	26.59	26.88	26.78	26.68	26.77	26.61
Lignin %	4.0	3.6	3.1	3.9	3.3	3.0	4.3	3.8	3.2	4.1	3.7	3.2
Ratio of lignin removal, %	92.89	93.77	94.87	93.12	94.51	95.13	92.83	93.80	94.96	93.31	94.16	95.08
Ratio of removed lignin to dissolved matters, %	27.15	27.03	26.75	27.09	26.73	26.59	29.34	29.33	29.16	29.18	28.96	28.86
Permanganate number	8.2	7.7	6.8	7.8	7.0	6.7	8.4	7.8	6.9	7.9	7.1	6.8
Ash %	0.22	0.20	0.18	0.21	0.18	0.16	0.21	0.19	0.17	0.20	0.17	0.15

* Based on original wood on oven dry basis.

Table-4					
Conditions of bleaching					
Stages		Chemicals as available Cl ₂ or, % alkali on o.d. pulp	Consis- tency %	Temp. °C	Retention time min
Chlorination	(C)	1.40-3	3	27 (RT)	30
Alkali Extraction	(E)	2	10	60	60
Hypochlorite	(H)	0.75-1.25	10	45	90
Alkali Extraction	(E)	2.0	10	60	60
Hypochlorite	(H)	0.75-1.15	10	45	60
Dil HCl treatment		0.05 (V/V)	4	27 (RT)	30

samples of cellulose were in the range 7.10-9.50 mg. Alpha-alumina was used as reference material and the temperature ranged from 30 to 800°C at heating rate 10°C min⁻¹, in static air atmosphere.

RESULTS AND DISCUSSION

The results of proximate chemical analysis presented in Table-1 indicate the suitability of Ekra and Khagra reeds for preparing high alpha-cellulose pulp. The pentosan in Ekra reed (20.35%) is a bit higher than that in the Khagra reed (19.42%), while the lignin is 19.23% and 20.70% respectively. The ash content in both the reeds (2.12 and 2.04%) are almost same.

The prehydrolysis was carried out at three different temperatures viz. 135, 145 and 155°C for 2.5 and 3h respectively. Table-2 gives the yields of prehydrolyzed chips, pH of prehydrolyzed liquors, ratio of pentosan and lignin removals etc. It is evident from the data that percentage removal of constituents like pentosan, lignin and ash from original material, increases with the increase in prehydrolysis temperatures, while increase of prehydrolysis time at certain temperature does not effectively increase the removal of these constituents. The ratios of pentosan and lignin removal percentages increase with increase in temperature and duration of prehydrolysis. It would be seen that the rate of hydrolysis is governed by temperature and time (15).

The sulphate cooking of prehydrolysed chips was carried out under the conditions as mentioned earlier. Time and temperature have significant effect on the reduction of pentosan, lignin, ash content etc. Fig.1 (a,b) and (c,d) show the effect of prehydrolysis temperatures on yield, pentosan and lignin removal of unbleached pulps at 2.5 and 3h prehydrolysis of Ekra and Khagra reeds respectively.

The Characteristics of bleached pulps obtained from the selected batches are presented in Table-5. The bleached pulp yields of 27.1-28.1% on the basis of original raw materials were obtained. Alpha-cellulose (92.5-94.8%) with acceptable brightness, D.P., pentosan and ash contents could be obtained, which compare well with that of standard viscose grade dissolving cellulose (17).

The alpha-cellulose obtained from batch 5 (Cellulose A) and batch 9 (Cellulose B) were analysed by IR, X-ray and thermogravimetric techniques and compared with the data obtained from similar analysis of a commercial rayon grade pulp (M/s Harihar Polyfibres, India), containing 95.5% alpha-cellulose and 0.05% ash (Cellulose C).

The comparative IR spectra of celluloses A, B and C (Fig.2) exhibit characteristic absorption bands of O-H stretching (3360 cm⁻¹), C-H stretching (2920 cm⁻¹), C-H bending (1380 cm⁻¹), -OH bending (1320 cm⁻¹) etc (18-20). Similarly, X-ray diffraction patterns of celluloses A, B and C (Fig.3) indicate that the celluloses are typical native cellulose having crystalline and amorphous regions (21).

The thermal curves (TG and DTG) for celluloses A, B and C are shown in Fig.3, at heating rate 10°C min⁻¹. The thermal analysis data in Table-7(a) show a major mass loss with maxima around 295 to 312°C for all the three celluloses. Table-7(b) gives initial, maximum and final temperatures of active decomposition represented at T₁, T₂ and T₃ respectively. The percentage mass losses (57.2-59.5) in the active decomposition range for all the three celluloses are more or less comparable. It may be inferred that three main degradation steps namely initiation, propagation and carbonization as suggested by earlier workers (22) are predominant for all the three celluloses.

Table-5

Analytical data on bleached pulps

Particulars	Ekra reed			Khagra reed		
	2	3	5	6	8	9
Prehydrolysis:						
Time, h	2.5	3	2.5	3	2.5	3
Temp, °C	145	155	145	155	145	155
Batch No.	2	3	5	6	8	9
Yield, * %	27.8	27.3	27.6	27.1	28.1	27.7
Alpha-cellulose, %	92.5	93.8	94.3	93.1	93.0	94.8
Bata-cellulose, %	2.81	2.63	2.68	2.54	2.90	2.65
Gamma-cellulose, %	0.63	0.51	0.61	0.49	0.66	0.53
Pentosan, %	2.55	2.47	2.50	2.32	2.64	2.36
Copper Number,	0.078	0.063	0.073	0.061	0.077	0.065
Ash, %	0.08	0.06	0.07	0.06	0.07	0.06
D.P. (average)	995	980	972	963	998	984
Carboxyl content, (m eq/100g)	-	-	3.32	-	-	3.25
Brightness, %	85	86	87	86	85	88

*Results on original wood on oven dry basis.

Table-6

Morphological characteristics of unbleached pulp fibres						
Characteristics	Ekra reed			Khagra reed		
	Maximum	Minimum	Average	Maximum	Minimum	Average
Fibre length, L (mm)	2.1	0.43	1.45	4.2	0.44	1.50
Fibre diameter, D, (μ m)	20.0	11.6	20.8	25.2	11.1	21.3
Lumen diameter, d, (μ m)	15.2	6.8	12.75	14.9	6.5	12.12
Cell wall thickness, W, (μ m)	5.4	3.8	4.02	5.8	3.5	4.15
Slenderness ratio, (L/D)	-	-	69.71	-	-	70.42
Runkel ratio, (2 W/d)	-	-	0.63	-	-	0.68
Flexibility co-efficient, (d/D x 100)	-	-	61.30	-	-	56.90
Wall fraction, (2 W/D x 100)	-	-	38.00	-	-	38.98
Ratio of cell wall thickness to fibre diameter, (2 W/D)	-	-	0.39	-	-	0.39
Ratio of cell wall thickness to lumen diameter (W/D)	-	-	0.32	-	-	0.34
Shape factor, $D^2-d^2/D^2 + d^2$	-	-	0.46	-	-	0.51

Table-7 (a)				
Thermal analysis data for celluloses at heating rate 10°C min ⁻¹				
Sample	DTG peak temperature (°C)			% weight loss
	I	II	III	
Cellulose A	83	295	414	57.2
Cellulose B	88	312	465	59.5
Cellulose C	100	300	-	57.5

Key : I, II, III --- pre, second and third stages.

Table-7 (b)			
Dynamic thermogravimetry data for celluloses at heating rate 10°C min ⁻¹			
Sample	Temperature of active decomposition (°C)		
	T ₁	T ₂	T ₃
Cellulose A	290	320	497
Cellulose B	310	328	545
Cellulose C	295	320	580

CONCLUSION

The physico-chemical properties of high alpha-cellulose extracted from *Erianthus longisetus* and *Neyraudia reynaudiana* exhibited identical properties to that of alpha-cellulose available commercially. Adopting water prehydrolysis at 145°C for 3h followed by sulphate pulping at temperature 163±2°C for 3h, with 17% active alkali as Na₂O at 20% sulphidity, good quality of alpha-cellulose could be produced from Ekra reed. So also similar results could be obtained from Khagra reed by prehydrolysing the chips at 155°C for 2.5h followed by identical conditions of sulphate pulping and multistage bleaching. From the experimental results, it may be concluded that Ekra and Khagra reeds could be ideal as raw materials for the production of high alpha-cellulose pulps.

ACKNOWLEDGEMENT

The authors are thankful to the Director, Regional Research Laboratory, Jorhat-785006, for his kind permission to present this paper in the Annual Meeting and Seminar organised by Indian Pulp and Paper Technical Association at Chennai during November, 1997.

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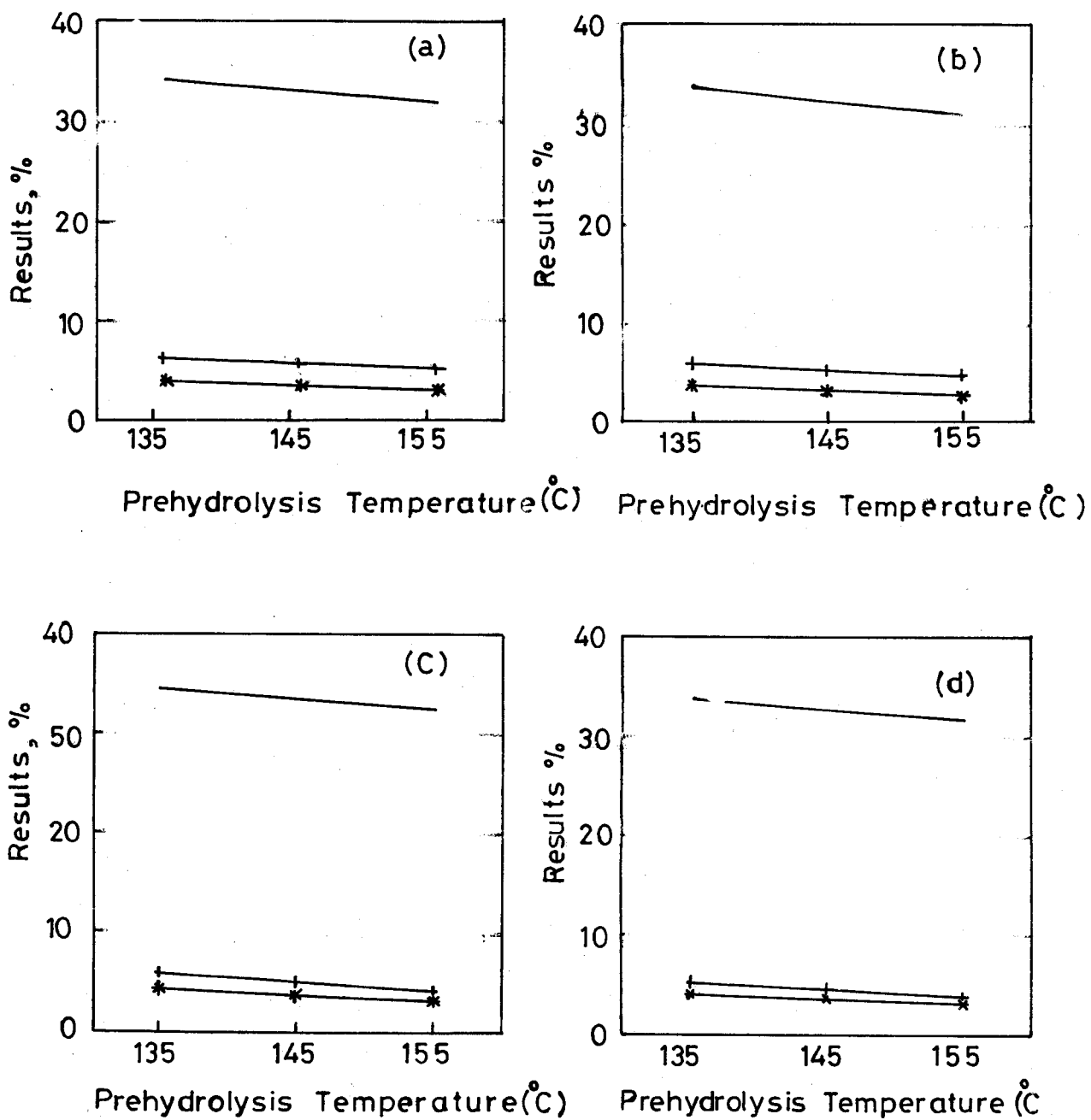


Fig-1

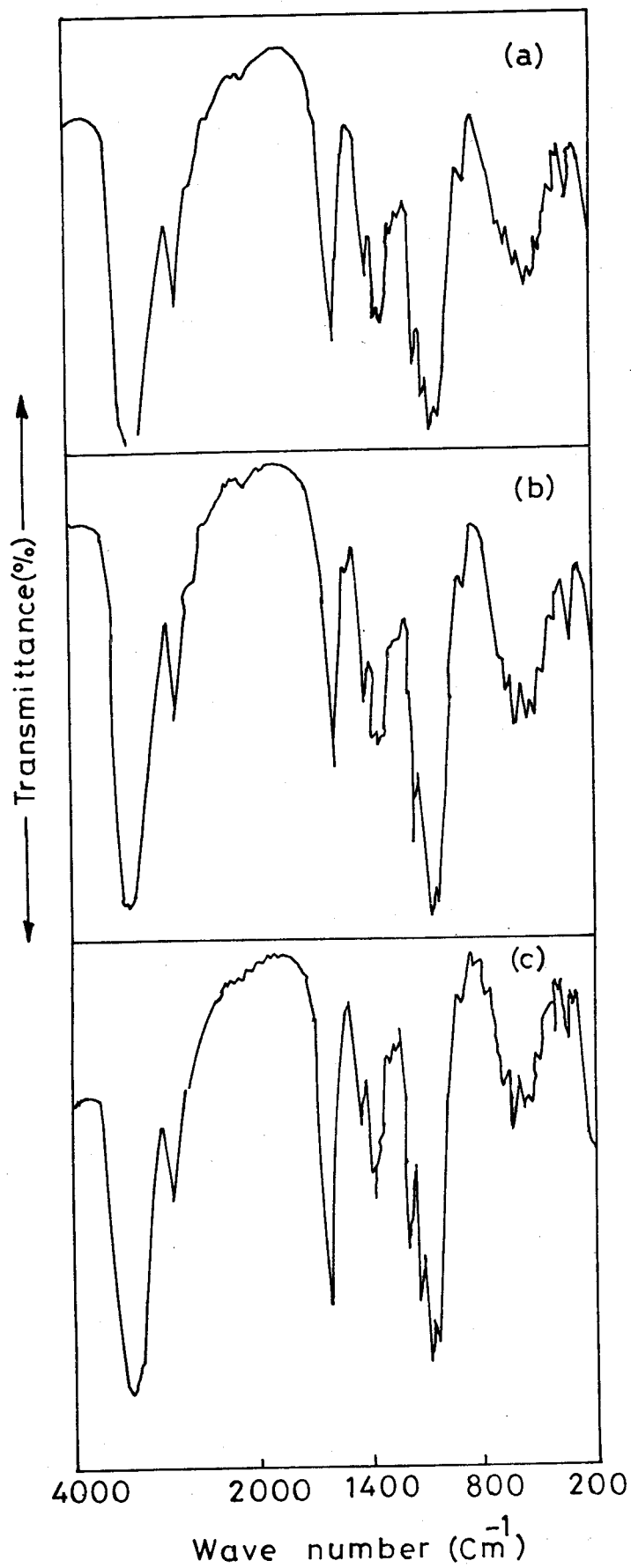


Fig-2.

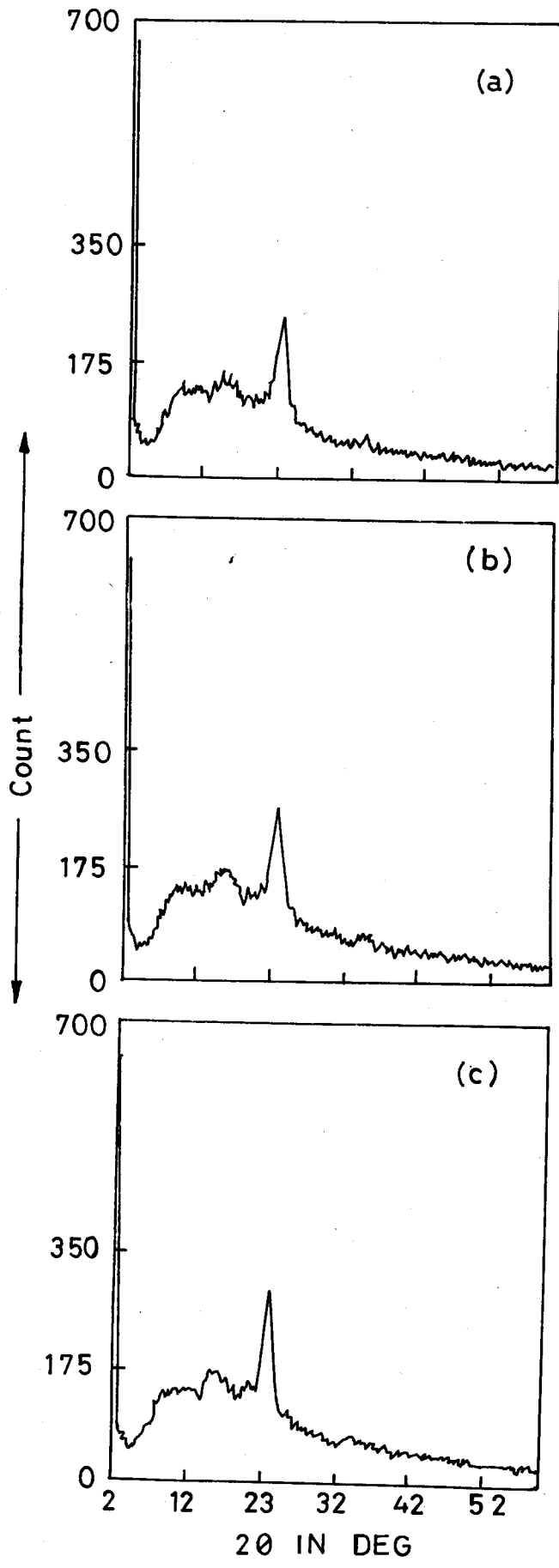


Fig-3

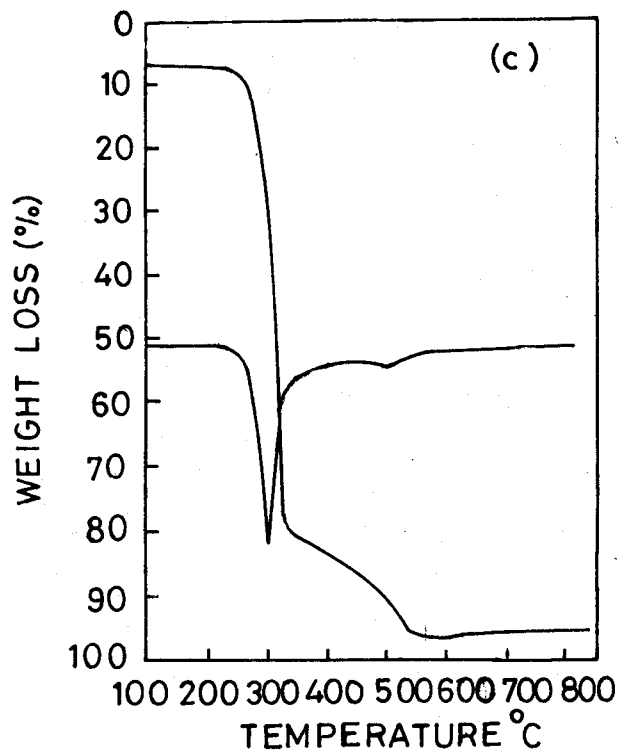
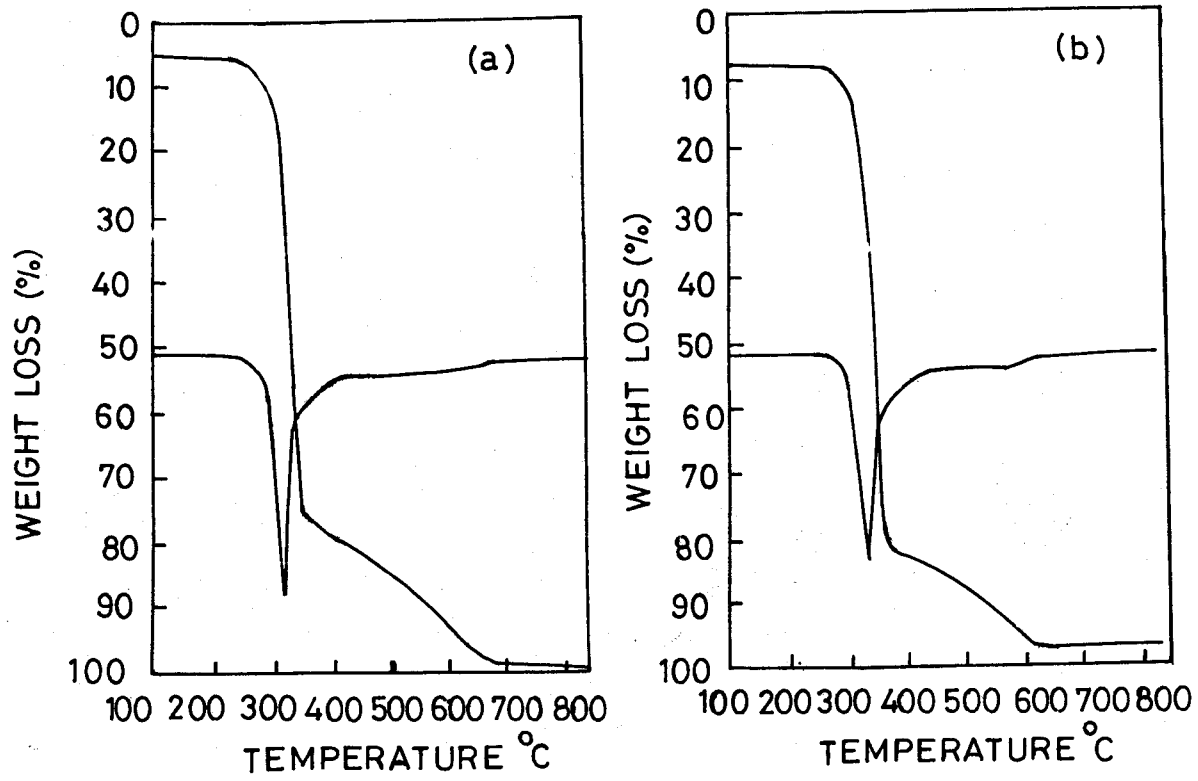


Fig 4.

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