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ORIGINAL ARTICLE

Trace the exploitation of Egyptian rice straw through spectral and thermal measurements

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Abstract Cellulose from rice straw obtained at low sodium hydroxide solution concentration with high quality was used to obtain different cellulose derivatives through xanthation. Cellulose was then treated with carbon disulfide in the presence of sodium hydroxide. The viscose obtained was characterized with both chemical and instrumental analyses, namely, IR spectra, TGA and DTA analysis as well as SEM (scanning electron microscopy).

1. Introduction

Production of cellulose from Egyptian rice straw could be attained through many methods known generally for the extraction of cellulose from its sources (Abou-Sekkina et al., 2010) and especially from rice straw (Changa et al., 2011). In this study, cellulose was obtained using a semi-chemical method (treatment of mechanically divided rice straw with sodium hydroxide). The produced cellulose was described using IR analysis (Isaa and Saad, 1978; Saad et al., 1980). Cellulose cannot be dissolved in water. Introducing hydrophilic groups along the chain of cellulose cleaves the hydrogen bonds and renders its derivatives soluble in conventional solvents, widening its applications to, for example, functional cellulose ethers and esters (Issa et al., 2009; Abdel Mohdy et al., 2009; Tappi Committee, 1999; AARC, 1997).

Commercial cellulose derivatives are either ethers or esters that are soluble in water or organic solvents. The three free hydroxyl groups in the AGUs react with various functional substitution groups. The resultant substituents therefore disturb the inter- and intra-molecular hydrogen bonds in cellulose, reduce the hydrophilic character of the numerous hydroxyl groups, and increase the hydrophobicity. Introducing ester and ether groups separates the cellulose chains almost completely so that the fiber structure is either altered or destroyed. The solubility of a cellulose derivative in a solvent or in water depends on the type of substituents, the degree of substitution and the molecular weight. These cellulose derivatives are grouped according to the processes and chemical substituents

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(British Columbia Pellet Fuel Manufacturers Association, 1997; California Air Resources Board and California Department of Food and Agriculture, 1997; Clean Fuels Development Coalition and American Bioenergy Association, 1998; Fibre Crete International, 1997; Mwaikambo and Ansell, 2002).

The technology of the synthesis of viscose from raw materials has certain problems (Stenius, 2000; Abdullaeva, 1993) connected with low rate of the process and impossibility of preparation of a product with high homogeneity on some qualitative indices. This is due to low reactivity and mass-diffusion of rice straw cellulose during the treatment with aqueous solution of sodium hydroxide. It has been established, as a result of experiments that, with the use of raw material mixtures for complete treatment of rice straw, the arising problems studied must be solved.

In the present research work, the experiments for the preparation of laboratory parts of cellulose pulps from rice straw were carried out. The obtained samples were allowed for IR spectra, TGA and DTA analysis as well as chemical analysis (permanganate number determinations) for comparison between xanthated and original samples. Scanning electron microscopy (SEM) was also employed for microstructural studies.

2. Experimental

2.1. Cooking conditions

In these tests, samples from rice straw were treated with NaOH solutions of different concentrations for different time periods at different temperatures.

2.1.1. Effect of sodium hydroxide concentration

Sodium hydroxide acts as a solubilizing agent for both silica and lignin found in raw materials. Samples (10 g) were boiled with 100 ml NaOH solution of certain concentrations (4%, 6%, 8%, 10% and 12%) for 2 h.

2.1.2. Effect of time at optimum alkalinity

Samples (10 g) were leached with 100 ml of 10% NaOH solutions and were boiled for different time periods (1, 2, 3 and 4 h).

2.1.3. Effect of weight/volume ratio

Samples (10 g) from rice straw were treated with 10% NaOH solutions while boiling for 2 h in different weight per volume ratios 1/5, 1/10, 1/20 and 1/50 (w/v).

2.1.4. Effect of cooking temperature on the yield of pulp

Samples (10 g) from rice straw were treated with 100 ml 10% NaOH solutions for 2 h at different degrees (40, 60, 80 and 100 °C).

2.1.5. Effect of the nature of rice straw on the pulp yield

Samples (10 g) from rice straw were treated with 100 ml of 10% NaOH solutions for 2 h at boiling point, length of samples used were the whole plant (80–120 cm length), 20 cm, 10 cm, 5 cm and mechanically divided plant (less than 1 cm).

2.2. Bleaching

The pulps produced by NaOH pulping are pale to intense yellow in color and require bleaching to reach acceptable brightness. The brightness of the bleached pulp depends on the bleaching sequences and conditions. So in this study the pulp was treated with sodium bisulfate solution (4% and 8%), and with sodium hydroxide solution (4%) then with hydrogen peroxide solution (4%) (Gustafsson and Peltonen, 2003).

2.3. Xanthation

Pulp (0.5 g) was exactly weighted, placed in a wide mouth bottle of 150 ml capacity, 100 ml of water was added to the pulp and it was allowed to swell in the closed bottle for at least 1 h. Fifty milliliters of NaOH solution (280.6/g/L), and 3.5 ml of carbon disulfide were added in this sequence, then the bottle was stoppered. The glass stopper must be fixed on the bottle as quickly as possible; the bottle was then shaken for 15 min and allowed to rotate in the thermostat at room temperature for 6 h.

2.4. Permanganate number (Nada et al., 1994)

It is a method of expressing the bleachability of pulp. It is determined by the number of mls of 0.1 N $KMnO_4$ consumed by one gram of moisture free pulp under certain specific conditions of time, temperature and acidity. Required volume of 0.1 N $KMnO_4$ (20–40 ml depending upon the rawness of the pulp) were paced in one beaker, an equal amount of 4 N H_2SO_4 is placed into another beaker and enough water combined with H_2SO_4, so that, the final reaction mixture of the permanganate solution will be 1/300 N. When the reagent is ready, the pulp specimen is added to the reaction beaker, followed by addition of sulfuric acid and then by addition of permanganate. After exactly 5 min at 25 °C an excess of KI is added to stop the reaction. The residual $KMnO_4$ in the mixture released an equivalent weight of iodine from the iodide salt solution. The liberated iodine is then titrated against standard sodium thiosulfate solution (Fahmy et al., 1979). The volume of permanganate consumed by the pulp is then calculated. The permanganate number is obtained by dividing the number of mls of 0.1 N $KMnO_4$ consumed by the moisture free weight of the test specimen; permanganate number $= \frac{25-V}{W}$ where V is the number of milliliters of 0.1 N $Na_2S_2O_3$ consumed in the titration, W is the weight of moisture free pulp and 25 is the number of ml of 0.1 N $KMnO_4$.

3. Equipments

IR absorption spectra were recorded as KBr discs within the 4000–200 cm^{-1} range on a Perkin Elmer 1430 infrared spectrophotometer. The thermal gravimetric analysis (TGA) was carried out on a Shimadzu TG 50 thermogravimetric analyzer from room temperature up to 1000 °C using 10 °C/min heating rate under nitrogen as atmosphere. The differential thermal analysis (DTA) was performed on a 990 Du-Pont differential thermal analyzer of 1200 °C cell using Al_2O_3 as a reference. The surface of rice straw and pulp from rice straw samples imaged with the (SEM) scanning electron microscopy type, JEOL JEM-850 operating at 35 kV employed in the Central Laboratory, National

Table 1 Assignments of bands in the IR spectrum of rice straw pulp (Lucia et al., 2000).

Wavenumber (cm^{-1})	Assignment	Wave number (cm^{-1})	Assignment
3600	νOH free	1475	δCH in pyran ring
3560	νOH (w) H-bond	1460	δCH_2 in pyran ring
3450	νOH (m) H-bond	1450	δCH_2 internal deform.
3380	νOH (s) H-bond	1435	δOH_3 and R-O-Ar ether
3250	νOH (s) H-bond	1385	δCH_2 external deform.
3100	νCH asym. aromatic	1340	δCH_2 external deform.
3050	νCH asym. aromatic	1285	δOH phenolic
2980	νCH asym. aliphatic	1270	δCH_2 external deform.
2960	νCH asym. aliphatic	1255	δCH_2 external deform.
2900	νCH sym. aliphatic	1235	δOH carboxylic
2880	νCH sym. aliphatic	1185	νC–OH phenolic
1750	C═O acetyl linkage	1165	δCH aromatic and C–O–C
1730	C═O β-keto structure	1140	νC–OH carboxylic
1675	C═O β-keto structure	1115	δCH aromatic
1630	δOH (water molecules)	1065	δCH aromatic
1610	C═C aromatic ring	1040	Lignin band
1595	C═C aromatic ring	800	C–O cellulose
1530	C═C aromatic ring		

Research Centre, Cairo, Egypt. Samples are investigated as it is without any change in their physical form.

4. Results and discussion

4.1. Analysis of raw materials and obtained cellulose pulp

Three samples from rice straw collected from different places in the El-Delta region, Egypt were subjected for analysis to determine the fibrous part of rice straw for each sample. The American Tappi standards were used in most of the chemical analyses of the raw materials and pulps involved in this work (Tappi Committee, 1999). The results obtained for different samples included in this study indicate that the moisture content varies from 10% to 12% and the presence of 10–12% of water soluble matters whereas the ash content was found to vary from 12% to 16%. The percentage of α-celluloses increases from 29% in the raw material to 90% in the obtained pulp.

4.2. Effect of cooking conditions

The results for different experiments described in the experimental part for this factor, reveals that cooking mechanically divided rice straw in 10% NaOH solution for 2 h with boiling and 1/50 (w/v) ratio are the best pulping conditions.

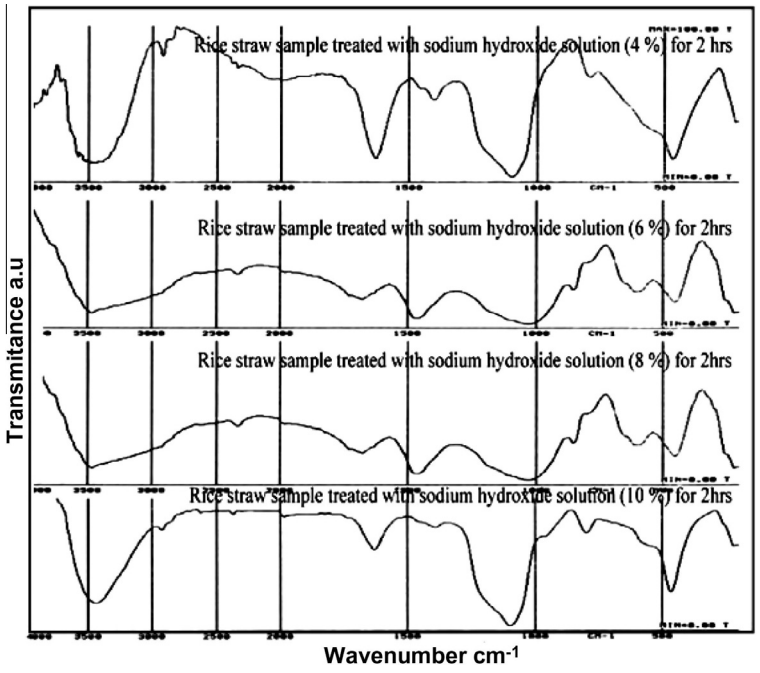

Figure 1 IR absorption spectra of soda treated rice straw samples.

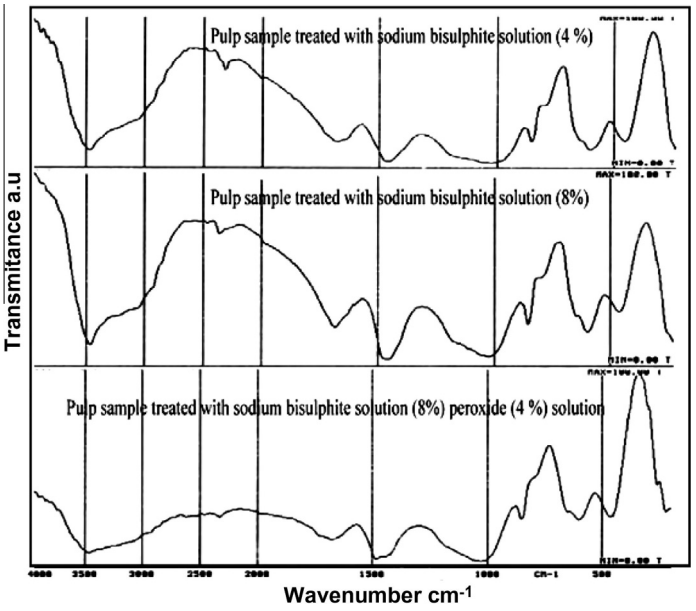

Figure 2 IR absorption spectra of bleached pulp samples.

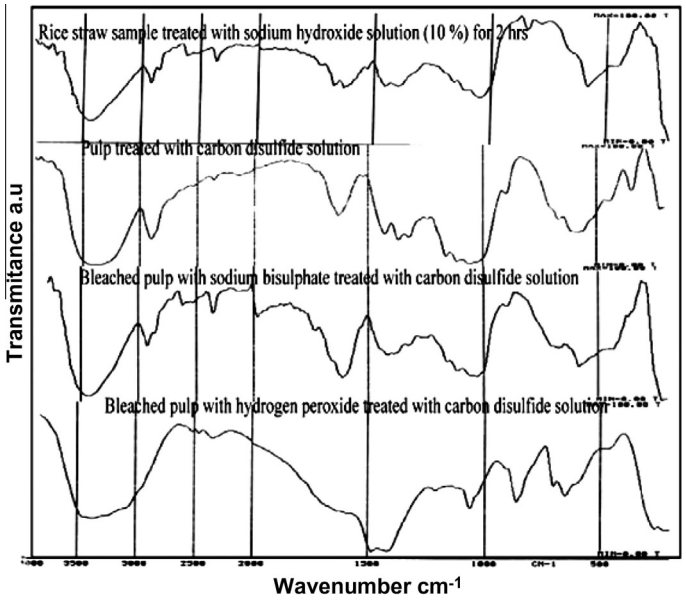

Figure 3 IR absorption spectra of xanthated cellulose samples.

4.3. Infrared spectrophotometric study of cellulose obtained from high yield soda rice straw pulps

Isaa and Saad (1978) and Saad et al. (1980) in an article on the silylation of cellulose gave a collective assignment for the infrared absorption spectra of different kinds of cellulose and tabulated the main important bands of each kind. This table is actually very beneficial for obtaining the assignments of IR bands of cellulose materials. Hence it is considered to be of great help for assigning the IR spectra of rice straw pulps obtained under different conditions of cooking the rice straw with sodium hydroxide solutions. The band assignments given by previous authors in many studies were helpful in obtaining the correct assignments for various bands in the IR absorption spectra of rice straw pulp samples obtained under different cooking conditions (Saad et al., 1980). The data obtained are collected in Table 1. In this point of our study we would discuss the assignments of bands in the IR spectra of Egyptian rice straw and the changes in the infrared spectra which take place during the pulping and xanthation processes. On comparing the spectrum of the obtained pulp samples under different conditions of treatment and xanthated cellulose samples (Figs. 1–3) the following can be pointed out:

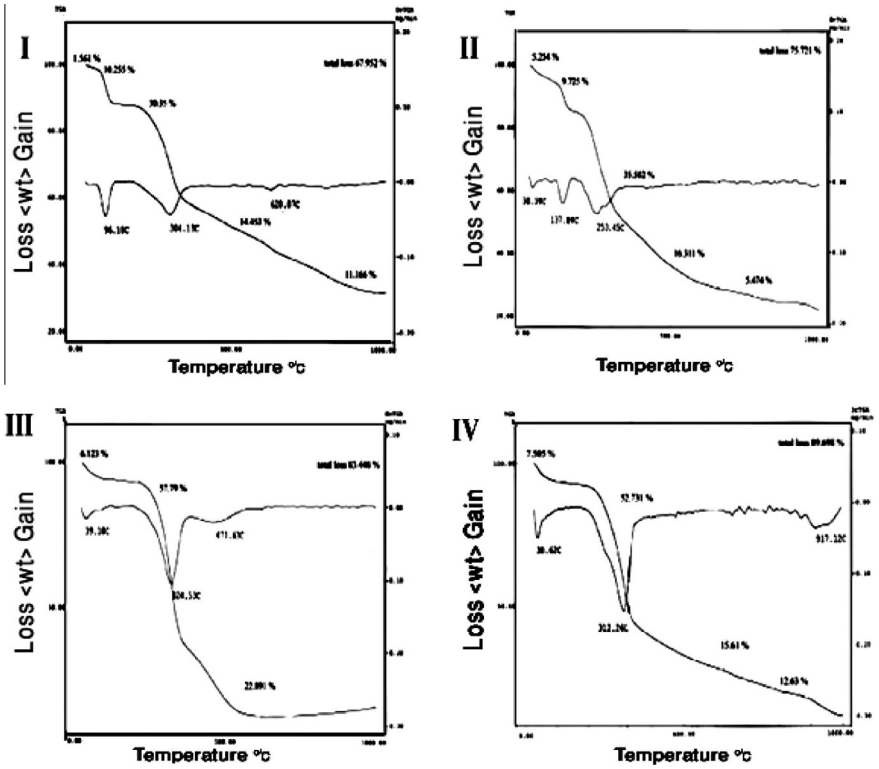

Figure 4 The TGA of sample I; rice straw pulped in sodium hydroxide solution (8%) for 1 h, sample II; rice straw pulped in sodium hydroxide solution (8%) for 2 h, sample III; rice straw pulped in sodium hydroxide solution (10%) for 2 h and sample IV; rice straw pulped in sodium hydroxide solution (10%) for 2 h and bleached with sodium bisulfate (5%) for 1 h.

Table 2 TGA analysis for cellulose samples.

Band	Weight loss (%)			
Temperature range	Sample I	Sample II	Sample III	Sample IV
35–100 °C	11.80	14.98	6.12	7.51
300–325 °C	30.35	35.58	57.79	52.73
470–1000 °C	25.62	21.79	22.89	28.24
Total weight loss	67.95	75.72	83.44	89.69
Remaining ash	32.05	24.28	16.56	10.30

(a) The broad δOH band at 1600 cm^{-1} tends to be less broad in the spectra of the pulps, meanwhile the band envelopes becomes more symmetrical. This is due to the dissolution of light celluloses especially α-cellulose in the cooking medium. The bands due to the stretching vibrations of the CH-groups tend to be sharper in the spectra of the pulps with the loss of absorption on the higher frequency side where the bands due to aromatic CH-groups appear. These changes reflect the dissolution of lignin materials on cooking with sodium hydroxide solution. The group of bands within the 1400–1200 cm^{-1} becomes sharper with the rise of either NaOH concentration or cooking temperature. The intensity of most bands decreases in the same direction while the peaks at 1630–1370 cm^{-1} tend to be sharp and display a slight increase in peak intensity. The bands within the 1200–900 cm^{-1} region tend to be less broad in the spectra of the pulps, yet the most obvious change in this region is the appearance of some sharp peaks near 1100 cm^{-1}. These changes recall more or less those observed with mercerization of cellulose and can be similarly accounted for (Gassan and Bledzki, 2001).

(b) The strong band at 1735 cm^{-1}, assigned to the stretching vibration of the C═O group of the acetyl residue from polyurinoid of the hemicelluloses, displays an obvious decrease in intensity when rice straw is cooked. The decrease of C═O band intensity and its vanishing in the spectra of the pulps is due to the hydrolytic rupture of the acetyl linkage between lignin and hemicellulose during the pulping of rice straw with NaOH.

(c) The bands at 1595–1600 cm^{-1}, which correspond to the skeletal vibrations of the aromatic rings of the lignin part, show a gradual decrease on increasing the cooking time or with rise of temperature and /or alkali concentration. The drop in the intensity of this band denotes that the lignin content of the pulps decreased during cooking with various degrees depending on the prevailing experimental conditions.

By the complete removal of lignin and hemicelluloses a dissolvable pulp is formed that is used for manufacturing of cellulose derivatives, such as, cellulose xanthate. In this work for derivatization of rice straw xanthation reaction was used in which the ONa groups of cellulose were converted to O═C(S)SNa groups, respectively. By this conversion some hydrogen bonds between cellulose chains are broken. The characteristic absorption bands of the phenyl ring of the benzyl group appear at 1700–2000 cm^{-1} region. The C═O to the

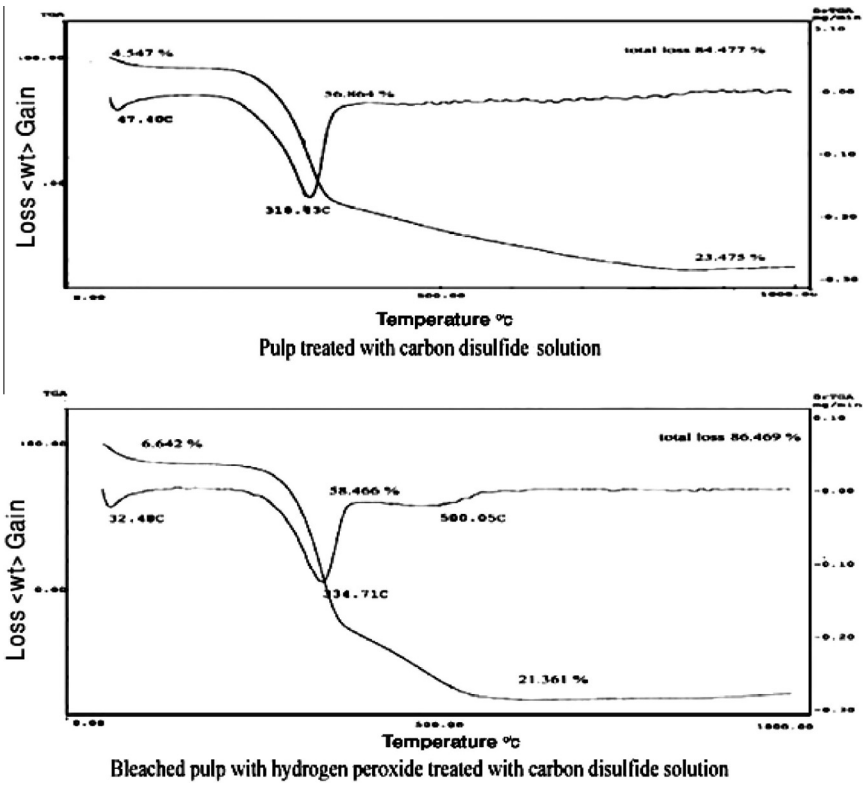

Figure 5 The TGA of xanthated pulp.

C═S occurs due to xanthation in addition to the C═O band itself which is more sharp and boarder for the sample (b), this may be due to bleaching with H_2O_2 as had been stated above which break some hydrogen bonds and freed more positions to be substituted.

4.4. TGA studies of cellulose pulp samples

The whole rice straw starts to degrade thermally at about 50 °C. Between about 300 and 375 °C, the majority of the carbohydrate polymers thermally decomposed and only the lignin remains. The hemicellulose components start to decompose at about 225 °C and are almost completely degraded by 325 °C. The cellulose polymer is more stable to thermal degradation until about 370 °C, whereas lignin starts to decompose at about 400 °C (Tutus and Eroglu, 2003).

Fig. 4 and Table 2 show that there are three different thermal loss stages. The first stages started at 25 °C and ended at 96.10, 30.39, 39.18, and 38.62 °C representing weight loss of 11.801%, 14.979%, 6.123% and 7.505% which can be attributed to the removal of moisture content from samples I, II, III and IV, respectively. The second stages at 304.13, 253.45, 324.53, and 312.26 °C, are suggested to be due to the thermal oxidation of the carbon content, its ratio reached, at 30.35%, 35.582%, 57.790% and 57.731% of the total sample weight for I, II, III and IV.

The third stages from above 470 °C to 1000 °C represent weight loss of 25.619%, 21.785%, 22.891% and 28.24% which are due to the complete oxidation of the remaining organic matter. Fig. 5 represents TGA and DTG thermographs of two samples of xanthated cellulose. There are two stages for both samples representing total weight losses of 84.48% and 84.28%, respectively. These two steps correspond to the thermal degradation of the organic part of the sample. The remaining residue is about 15.5%.

4.5. Differential thermal analysis (DTA) studies of cellulose pulp samples

In Fig. 6, there is an endothermic peak at 90 °C which can be due to loss of moisture content, and there are two exothermic

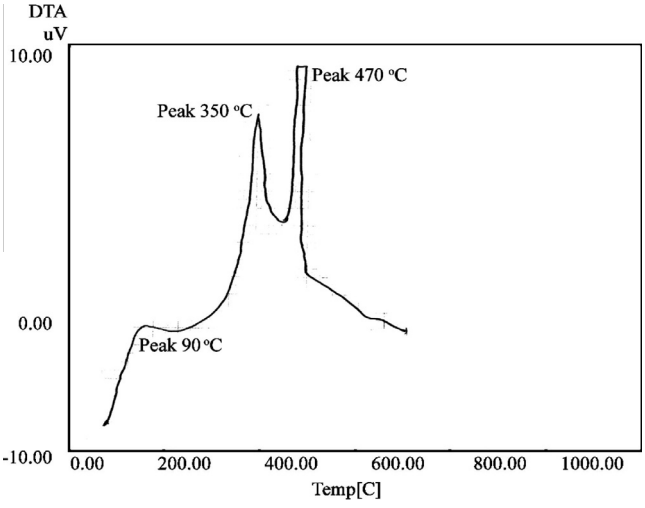

Figure 6 The DTA thermograph of cellulose sample prepared from rice straw by pulping in soda (10%) for 2 h.

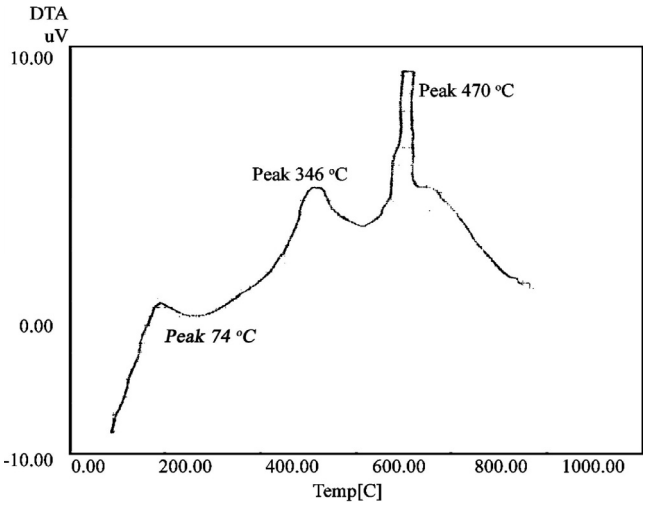

Figure 7 The DTA thermograph of xanthated cellulose sample.

peaks at 350 and 470 °C which are due to oxidation reactions of cellulose pulp, which is composed mainly of carbon, hydrogen and oxygen which oxidizes both carbon and hydrogen and this oxidation is an exothermic reaction.

Fig. 7 displays an endothermic peak at 74 °C which represents content loss, and there are two exothermic peaks at 346 and 470 °C which are assigned to oxidation of carbon content and complete oxidation of that carbon.

4.6. SEM investigation

SEM is a powerful and good technique to image fibers in micrometer scale. The physical trends like the removal of fines and fillers, or the different nature of hardwood and softwood fibers can be visualized with SEM. Surface scanning with the electron microscope was used to compare between the obtained cellulose pulp samples (El-Saied and Nada, 1993). The supermolecular structure of the blank (mechanically divided rice straw), treated with sodium hydroxide, sodium sulfite and H_2O_2 bleached samples as well as xanthated cellulose samples were studied by electron microscopy (Fig. 8). In case of the thermally treated samples the fibril bundles become similar and there is a gradual decrease in voids between cellulosic fibers as a result of dehydration, taking place during the heat treatment (aging) and the pulp crystallinity increases during this process. When the samples were treated with different concentrations of alkali, the fibers tended to agglomerate gradually into small and large bundles (Fig. 8).

Fig. 8 indicates that many bundle aggregations show the decrease in voids between them which confirms the increase in the degree of polymerization and crystallinity. On increasing the time of pulping and increasing alkali concentration, the degradation products become more pronounced with large spaces between them as in the case of 10% alkali treated pulps, the appearances are most likely tiny degraded products which have been removed during the fracture of the pulp surface. Fibers of the bleached cellulose samples are more arranged and

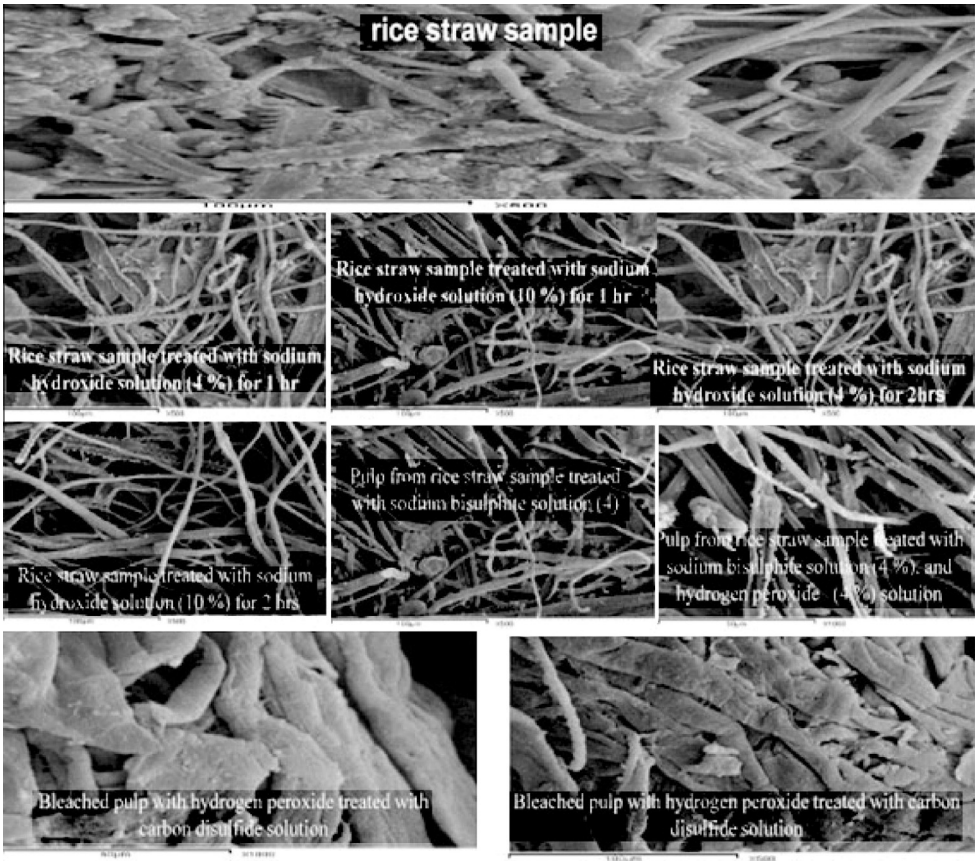

Figure 8 SEM of rice straw pulp samples.

the crystallinity increased due to the loss of fine (soluble low molecular cellulose and lignin products). Evidence of surface roughness can be seen using SEM. In addition, porosity and pore size on the fiber surface was found to increase with increasing treatment with sodium bisulfate and hydrogen peroxide. For xanthated pulp samples, the inhomogeneity of the pulp can be observed. The diameter of fibrils becomes heterogeneous. The void of the fibrils was randomly distributed. The aggregated micro fibrils are also randomly distributed. The inhomogenity will lead to the inhomogeneous xanthation reaction in the total fibrils. The inhomogeneous xanthation will lead to poor solubilities of synthesized xanthates.

5. Conclusion

Egyptian rice straw can provide high quality cellulose pulps and was found to be suitable for synthesizing high molecular weight xanthates. The xanthates, which were synthesized in an ordinary apparatus, had sufficient and different properties to compare plant species, process parameters of pulping and bleaching. Therefore, this method is appropriate for evaluating whether certain plants could be used to produce xanthated cellulose. Thus, it is feasible and appropriate to produce xanthates from rice straw. The pulping conditions were the key factors in the production of pulps and xanthates. However, the cellulose pulps obtained from rice straw are decisive factors for the preparation of xanthates. From the results obtained by different measurements in this work we can conclude that, the method used in this work is a good way to use this undesired waste to obtain very important products in our life (cellulose pulp for different uses).

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