

PREPARATION AND CHARACTERIZATION OF MICROCRYSTALLINE CELLULOSE (MCC)

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Cotton linters were hydrolyzed with different concentrations of HCl (2.5-15%) to prepare microcrystalline cellulose. Infrared spectroscopy and thermal analysis were used to follow the effect of hydrolysis on the molecular structure of the produced microcrystalline cellulose. The loss in weight and the degree of polymerization of the produced hydrolyzed cotton linters were determined. Scanning electron microscope images and x-ray diffraction were also studied for more information about the crystallinity, fiber length, particle size, and shape of the produced microcrystalline cellulose. Water retention value and water absorption were estimated for the hydrolyzed cotton linters to explain the effect of hydrolysis on the amorphous and crystalline part of the hydrolyzed cotton linters. The obtained results showed that the crystallinity index of the hydrolyzed cotton increased by increasing acid concentration and then began to decrease at 15% HCl. Kinetic energy (calculated from thermogravimetric curves) of the hydrolyzed cellulose was higher than that of the untreated cotton linters, and at high acid concentration this activation energy began to decrease.

Keywords: Cotton linter; Microcrystalline cellulose; Infrared, Thermal analysis; Scanning electron microscope; Kinetic energy; Water retention value.

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INTRODUCTION

Cellulose is one of the most important substances among natural and synthetic polymeric materials. Fibrous cellulosic materials are capillary porous disperse systems with high specific surface areas.

Cellulose raw material has been treated chemically to prepare mainly low molecular weight products, in addition to cellulose ether or esters (Mirkamlov and Sultanove 2000). Cellulose of low molecular weight can be prepared by hydrolysis in two steps. In the first step the amorphous parts of cellulose are mainly hydrolyzed, and what remains is the dense cellulose of 100-200 D.P., which has up to 80% crystallinity. In the second step, these dense cellulose domains are hydrolyzed under harsher conditions (Hakansson and Ahlgren 2005). The change in the degree of polymerization (DP) as well as the dissolution of cellulose during the hydrolysis process may be useful factors providing a further understanding of the rearrangement of cellulose in microfibrils of the original cellulosic fibers. A series of studies were carried out to recognize the molecular structure of the hydrolyzed and unhydrolyzed cellulose e.g., infrared spectroscopy and

thermal analysis tools (Nada et al. 2000). A series of studies were published on the application of the produced microcrystalline cellulose (MCC) and its uses in different fields. Some of these applications are mainly in food, cosmetic, and medical industries, where the MCC can function as a water retainer, a suspension stabilizer, a flow characteristic controller in the system used for final products, in preparation of gels formation, as ion exchangers (Nada and Hassan 2003, 2006), or as a reinforcing agent for final products such as medical tablets (Tobyn et al. 1998; Yokata and Okumura 1985).

A mechanism for liquid-phase degradation and hydrolysis has been suggested, in which the fibrils are cut (Gurnagul 1992). According to several investigations of heterogeneous hydrolyses of cellulose, DP decreases rapidly until it reaches a so-called “leveling off” degree of polymerization (Krassig 1993; Browning 1967).

The aim of this study was to hydrolyze cotton linters with different HCl concentrations (2.5-15%) under reflux to prepare MCC. The characterization of the produced MCC was studied using infrared spectroscopy (IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), and thermal analysis. The degree of polymerization (DP) of the hydrolyzed cotton linters was also investigated. Moreover, the water retention value, the water absorption, and the gel formation for the produced MCC were determined.

EXPERIMENTAL

Raw Material

The cellulosic material used in this study was cotton linters of 99.1% α -cellulose. It was delivered from Factory 18, Abu-Zaabal, Egypt.

MCC Preparation

Cotton linter was hydrolyzed with different hydrochloric acid (HCl) concentrations (2.5 to 15%) under reflux for one hour; the liquor ratio was 1:100. The hydrolyzed cotton linters were thoroughly washed with distilled water and dried.

The degree of polymerization (DP) of the produced hydrolyzed cotton linters was determined according to (Glockner et al. 1968).

The water retention value (WRV) of the produced MCC was determined according to Jayme (1958).

Infrared Spectroscopy

Infrared spectroscopy of the untreated and treated cotton linters was determined with a JASCO F7/ IR 300 E- Fourier Spectrometer Transform Infrared, using the KBr disc technique.

X-ray Diffraction Studies

Diffraction patterns were obtained using a Phillips X-ray diffractometer. The diffraction patterns were recorded using Cu-K α radiation at 40 KV and 25 mA. The samples were pressed into pellets (25 mm in diameter) by compression of 0.25 g in a mold under a pressure of 50 MPa. The crystal size of MCC was measured using the half-

height width of the I_{002} reflection, and the crystalline index (CrI) was calculated as follows (Segal et al. 1959),

$$CrI = [(I_{002} - I_{am})] / I_{002} \quad (1)$$

where I_{002} is the intensity of the 002 peak (at about $2\theta = 22^\circ$ - 24°) and I_{am} is the intensity corresponding to the peak at about $2\theta = 18^\circ$.

Thermogravimetric Analysis (TGA)

Thermal analysis was recorded with a Perkin Elmer Thermogravimetric analyzer, Thermal analysis Controller TAC 71DX TGA7 using a rate of heating of $10^\circ\text{C}/\text{min}$, in nitrogen atmosphere, with a rate of flow of $50\text{ cm}^3/\text{min}$.

Scanning Electron Microscopy (SEM)

The SEM of the samples (gold coating, Edwards Sputter coater, UK) was performed using a Jeol 6310 (Jeol Instruments, Tokyo, Japan), 840A Electron Probe Micro analyzer, with the system running at 5-10 keV.

RESULTS AND DISCUSSION

Infrared Spectroscopy

The molecular structures of hydrolyzed and unhydrolyzed cotton linters were characterized by infrared spectroscopy.

Figure 1 shows the spectra of untreated cotton and cotton treated with different acid concentrations. Table 1 shows the relative absorbance (ratio of any band intensity to the band intensity at wavenumber 1325 cm^{-1} that corresponds to CH rocking of the ring) (Yu Levdek et al. 1967) and crystallinity index (ratio of band intensity at wavenumber 1425 cm^{-1} to band intensity at wavenumber 900 cm^{-1}) (Nelson and O'Connor 1964) of hydrolyzed and unhydrolyzed cotton linters.

Table 1. Relative Absorbance and Crystallinity Index of Treated and Untreated Cotton Linters

Acid Treated %	Band Wavenumber	Relative Absorbance			Crystallinity index
		-OH 3435 cm^{-1}	CH_2 2920 cm^{-1}	Ether Band 1120 cm^{-1}	
Zero	3419	1.78	0.66	1.42	1.49
2.5	3342	1.29	1.08	1.21	1.62
5	3342	1.20	1.08	1.04	1.64
10	3340	1.09	1.07	1.10	1.59
15	3340	1.08	1.02	1.15	1.52

From Table 1 it is clear that the relative absorbance of OH groups at 3419 cm^{-1} was decreased by increasing the acid concentration ratio used in the hydrolysis process. This can be attributed to the decrease in the amorphous region, which is the first part hydrolyzed and degraded by acid. On the other hand, the relative absorbance of the CH_2 group at 2920 cm^{-1} of hydrolyzed cotton linters was increased by increasing acid concentration. This is attributed to the decrease of CHOH (secondary OH group) in the amorphous region by acid hydrolysis. So, the OH group in the position 6, which is attached with an CH_2 group, increased. The effect of hydrolysis of cotton linters with different concentration of acid on the relative absorbance of CH_2 was nearly the same.

The relative absorbance of the 1-4 ether linkage between glucose units at 1120 cm^{-1} was also decreased by acid hydrolysis due to the degradation of the amorphous part of cellulose chains. From Table 1, it is seen that the relative absorbance of ether linkages at 1120 cm^{-1} decreased by increasing acid concentration due to the degradation of the amorphous part of cellulose chains, which caused a decrease in the ether linkage. By increasing acid concentration more than 5%, the relative absorbance of ether linkage band increased. This means that the use of higher acid concentration caused a degradation of the amorphous region, which increased the relative absorbance of ether linkage band and at the same time it affected the glucose units and the hydrogen bonds between crystalline cellulose. Consequently, the relative absorbance of the ether linkage band increased by hydrolysis of cellulose at higher acid concentration. The crystallinity index of the hydrolyzed cotton linters increased by increasing the acid concentration due to the degradation of the amorphous parts.

Also, as in the case of the relative absorbance of the ether linkage, the crystallinity indices had the same trend, i.e., they increased with increasing acid concentration up to 10%, and at 15% the crystallinity indices were slightly decreased. This proves that the high acid concentration not only had an effect on the degradation of the amorphous parts, but also caused a degradation of the glucose and hydrogen bond between the hydrolyzed cellulose chains. Also, the increase in the crystallinity index by acid hydrolysis can be attributed to the increase of the hydrogen bonding between the cellulose chains. This can be confirmed by the shift that occurs in the OH band at wavenumber 3419 cm^{-1} of the untreated cotton linters to the low wavenumber at 3340 cm^{-1} for the hydrolyzed cotton linters (Nelson and O'Connor 1964).

From Table 2, it can be noticed that the loss in weight was increased with low percent acid concentrations rising from 2.5 to 10.0. A high increase in loss of weight was obtained by increasing the acid concentrations from 10 to 15%.

The weight loss upon hydrolysis has earlier been used to assess the amount of disordered regions in the cotton linters. The weight loss upon hydrolysis is prior to the leveling of degree of polymerization (LODP), and as shown in the Table 2, the degree of polymerization (DP) of the hydrolyzed cotton linters was decreased by increasing the acid concentration.

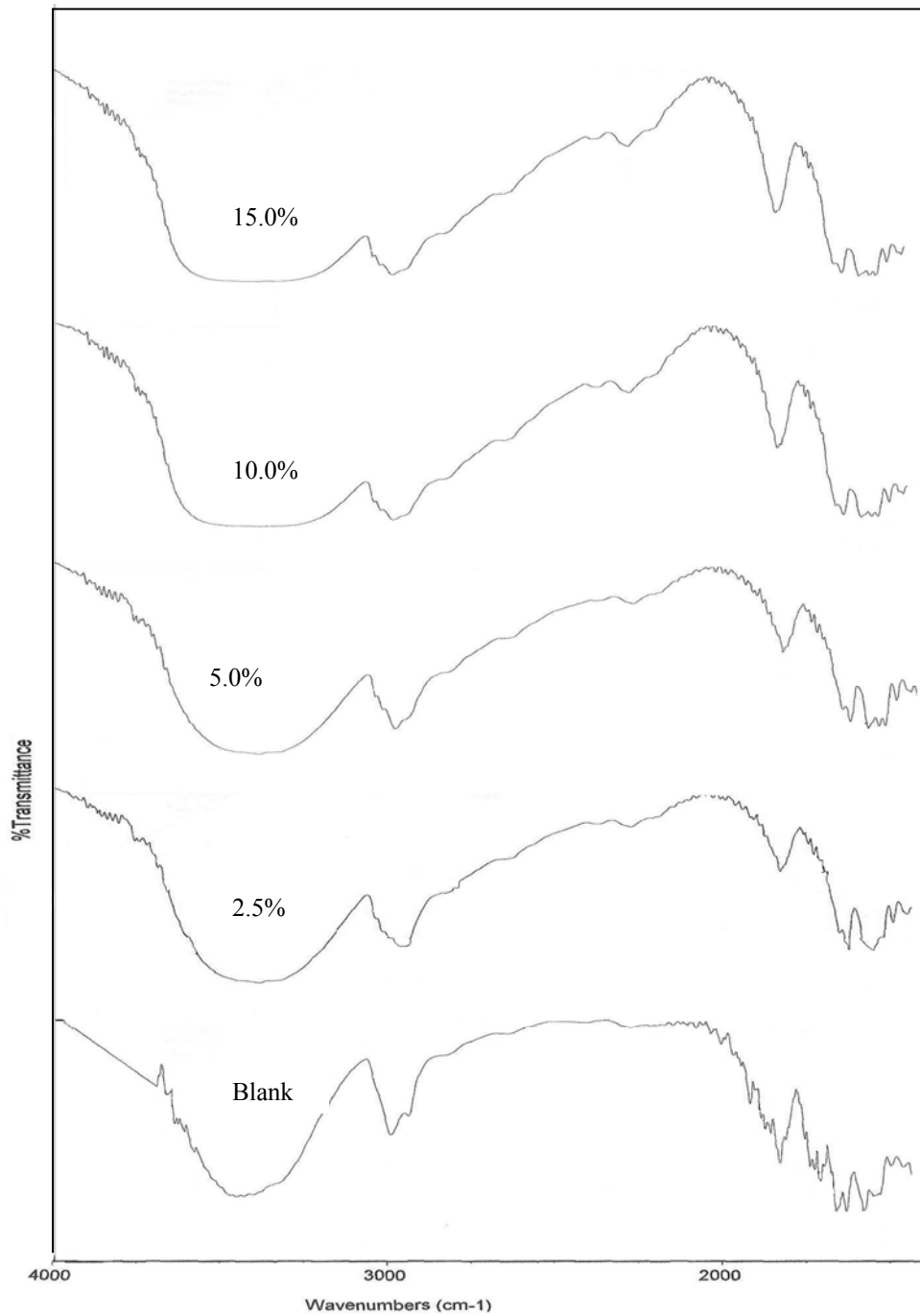


Fig.1. IR spectra of untreated and treated cotton linters with different concentrations of acid

Table 2. Effect of Acid Concentration on the Loss of Weight Percent of Hydrolyzed Cotton Linters

	Untreated Cotton Linters	Acid Concentration %			
		2.5	5.0	10.0	15.0
Loss in weight %	---	4.1	6.1	7.1	13.1
DP.	920	730	350	250	150

X-ray Diffraction

To give more information about the effect of acid hydrolysis of cotton linters with different concentrations of HCl between 5 and 15% for one hour, the x-ray diffractometer was used to determine the percent crystallinity of the hydrolyzed cotton linters. X-ray diffraction patterns were recorded by the reflection method. The diffractogram of cellulose showed two peaks with 2θ -range $21-23^\circ$ corresponding to crystallographic forms of cellulose and broadened peaks with 2θ range $15-19^\circ$. The value of 2θ angle at which the given peaks were observed changed during cellulose hydrolysis. The crystallinity of cellulose was estimated according to Segal et al. (1959), using Equation 1.

In our experiment, the hydrolyzed cellulose had much higher crystallinity than the unhydrolyzed cellulose (Table 3).

Table 3. X-ray Diffraction of Hydrolyzed and Unhydrolyzed Cotton Linters

	Position of 2θ		Crystallinity %
	001	002	
Untreated cotton liners	17.64 / 175.19	26.54 / 743.57	77.80
Hydrolyzed cotton liners 5%	17.27 / 263.04	26.39 / 1134.4	76.02
Hydrolyzed cotton liners 15%	17.04 / 269.00	26.40 / 956.76	71.40

From Table 3, it is clear that the crystallinity index of hydrolyzed cellulose had a lower value than the untreated cellulose. The 5% acid hydrolysis had a slight effect on the decrystallization of cotton linters, while upon increasing the acid concentration to 15%, the decrystallization of cotton linters was high. Also due to the decrystallization of cotton linters the peaks of X-ray diffraction were shifted to higher values of 2θ .

From previous discussion, it is clear that the obtained results from infrared spectra, X-ray diffraction, and DP followed the same trends, i.e. by hydrolysis, the calculate crystallinity indices were decreased by increasing the acid concentrations. This also was seen in case of X-ray diffraction and degree of polymerization.

Thermal Properties of Hydrolyzed Cotton Linters

Thermogravimetric curves of untreated cotton linters and hydrolyzed cotton linters with 5% and 15% HCl are shown in Fig. 2. From this figure it is apparent that the loss of weight occurred during heating of the sample in the range $100-120^\circ\text{C}$, which is

related to the moisture content of the samples. This loss was nearly equal to 6.5, 5, and 4.5% for cotton linters, vs. hydrolyzed cotton linters with 5% and 15% HCl, respectively. After the removal of moisture from the cellulosic material, the loss in weight of the cellulosic material increased due to the actual pyrolysis at minor decomposition temperatures of 275, 285, and 265 °C for the untreated and treated cellulosic material (Table 4).

Table 4. Minor and Major Decomposition Temperature of the Unhydrolysed and Hydrolysed Cotton Linters

Material	minor decomposition temperature °C	Loss in weight%	major decomposition temperature °C	Loss in weight %
Cotton linters	290	10	310	85
Hydrolyzed 5%	285	8	320	80
Hydrolyzed 15%	295	8	315	82

It is clear from Table 4 that the initial decomposition temperature as well as loss weight percent of the hydrolyzed cotton linters with 5% HCl was lower than the untreated and cotton linters hydrolyzed with 15% HCl. This can be attributed to the degradation of linkages between glucose units and some regions. On the other hand, the loss of weight of this hydrolyzed sample with 5% HCl had a lower value than other samples; this can be attributed to the decrease of the disordered regions and increase of the hydrogen bonds in the crystalline regions. The region of minor decomposition temperature and lower weight loss percent at this temperature for the hydrolyzed cotton linters with 15% acid is due to the degradation, which occurred in the glucose units in the cellulose chains. On the other hand, the changing temperature and loss weight percent of the hydrolyzed cotton linters with 5% HCl was higher than untreated cotton linters and linters hydrolyzed with 15% HCl. Generally, the microcrystalline cellulose of higher weight and crystalline regions were formed by hydrolysis at lower acid concentration, but at higher concentration of acid the microcrystalline cellulose with low molecular weight and crystals was produced. This agrees with the value of crystallinity index, in which it increased by hydrolysis of cellulose with low acid concentration (Fig. 2). Otherwise, increasing the acid concentration to 10% or 15% produced microcrystalline cellulose with lower crystallinity index and weight than that produced from 5% HCl, as shown in Tables 1 and 2.

Differential Thermal Analysis

It is clear that the curves for untreated cotton linters had three exothermic peaks at about 110 °C due to the evaporation of moisture and at about 315 °C, which is due to pyrolysis and degradation of small chains of carbohydrate and amorphous part, and finally at 416 °C, which is due to the decomposition and combustion of the crystalline part. In case of the hydrolyzed cotton linters with 5% and 15% acid concentration, two peaks were found, the first one at about 110 °C, which is attributed to the loss of moisture content, and the second peak at 304 °C and 295 °C for hydrolyzed cotton linters with 5% and 15% HCl respectively, which is due to the pyrolysis and decomposition of the

formed microcrystalline cellulose. Microcrystalline cellulose produced from cotton linters hydrolyzed with 15% HCl had peaks with decomposition temperature lower than that in case of that produced from hydrolysis with 5% HCl.

These results can be attributed to the degradation and decomposition of the formed microcrystalline cellulose. On the other hand, the peak height at the maximum decomposition rate of untreated cotton linters, which can be expressed as ΔG (Laszkiewicz. and Domasik 1989), was higher than the hydrolyzed cotton linters (as shown in Fig. 2). Also, the value of ΔG in the hydrolyzed cotton linters with low acid concentration was higher than that of hydrolyzed cotton linters with high acid concentration (Table 5).

Table 5. Decomposition Temperature and Kinetic Energy of Untreated and Hydrolyzed Cotton Linters with HCl

Samples	D.P.	Peak μ mp	Area	ΔG	Kinetic energy
Cotton linters	920	315.1	56.29	65.5	143
		416.2	10.3	21.5	----
Hydrolyzed 5%	350	304.5	71.2	74.1	114.8
Hydrolyzed 15%	150	295.5	76.2	78.2	100.25

Kinetic Energy

The data obtained from TGA curves were analyzed to calculate the kinetic energy. The value $\ln (W_0 - W_\infty / W_t - W_\infty)$ was plotted against time (t), where W_0 is the initial weight, W_t weight at time t , and W_∞ is the weight of ash. The slope of the obtained line is the rate constant for the thermal decomposition (Glastone 1962).

From Figure 3, it is evident that the relation between $\ln (W_0 - W_\infty / W_t - W_\infty)$ against time (t), under thermal conditions gave two linear parts. The first part occurred over the initial 25 min, due to the loss of moisture, and the second was due to the thermal decomposition; i.e., the loss in weight was first order. Kinetic energies were calculated from these curves and are collected in Table 5.

From this Table, it is clear that the kinetic energy of untreated cotton linters had higher activation energy than that of the hydrolyzed one. The hydrolyzed cotton linters had a lower kinetic energy than the untreated sample. This can be attributed to the degradation that occurs in the cellulose chain and the consequent decrease of the degree of polymerization. On the other hand, the hydrolyzed cotton linters with high concentration of HCl (15%) had a lower kinetic energy than those treated with lower concentration. This is due to the decrease in the crystallinity and the more degradation in cellulose chain, which enhanced the decrease in the degree of polymerization.

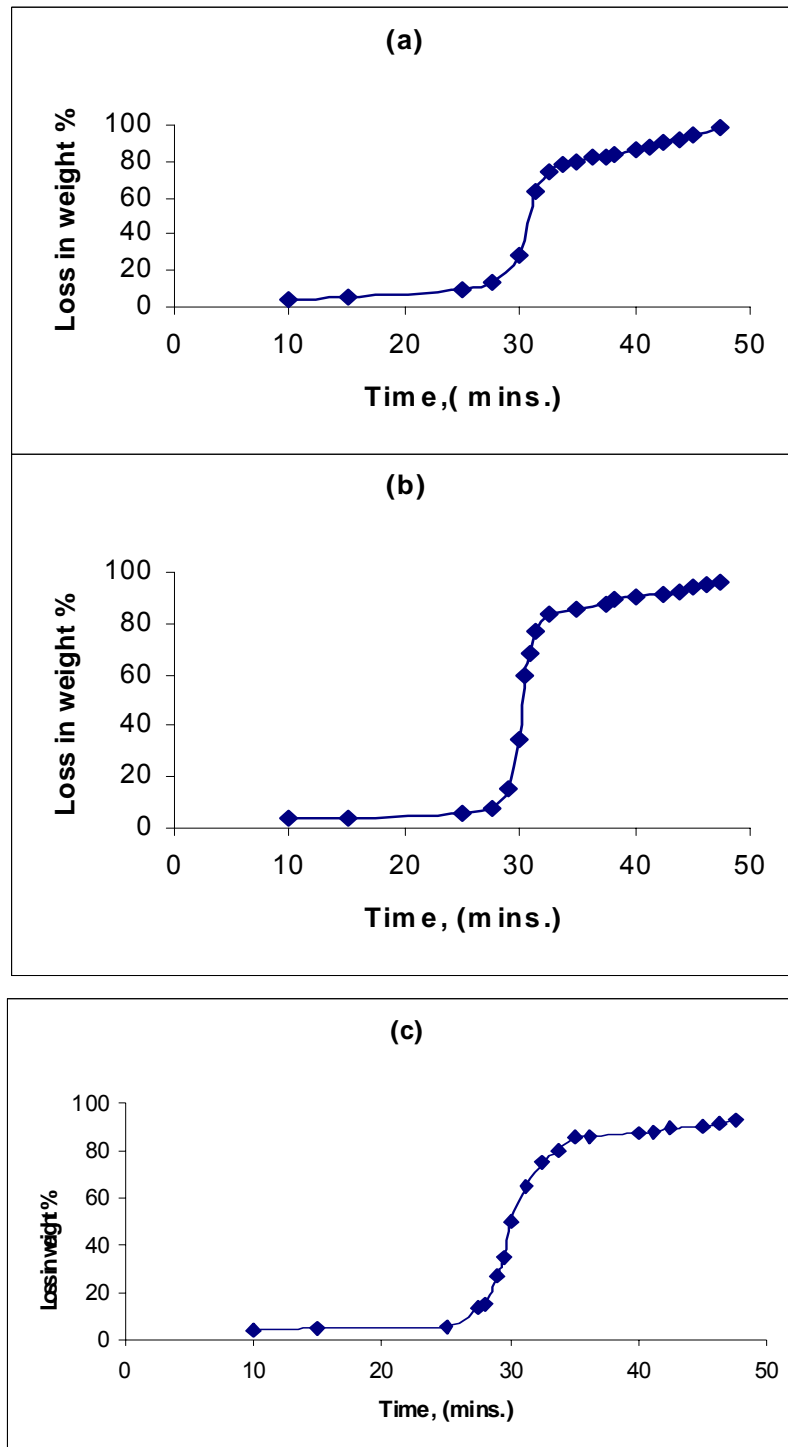


Fig. 2. TGA, relation between loss in weight % and time (mins.) of (a) untreated cotton linters, (b) hydrolyzed cotton linters with 5 % HCl, and (c) hydrolyzed cotton linters with 15 % HCl

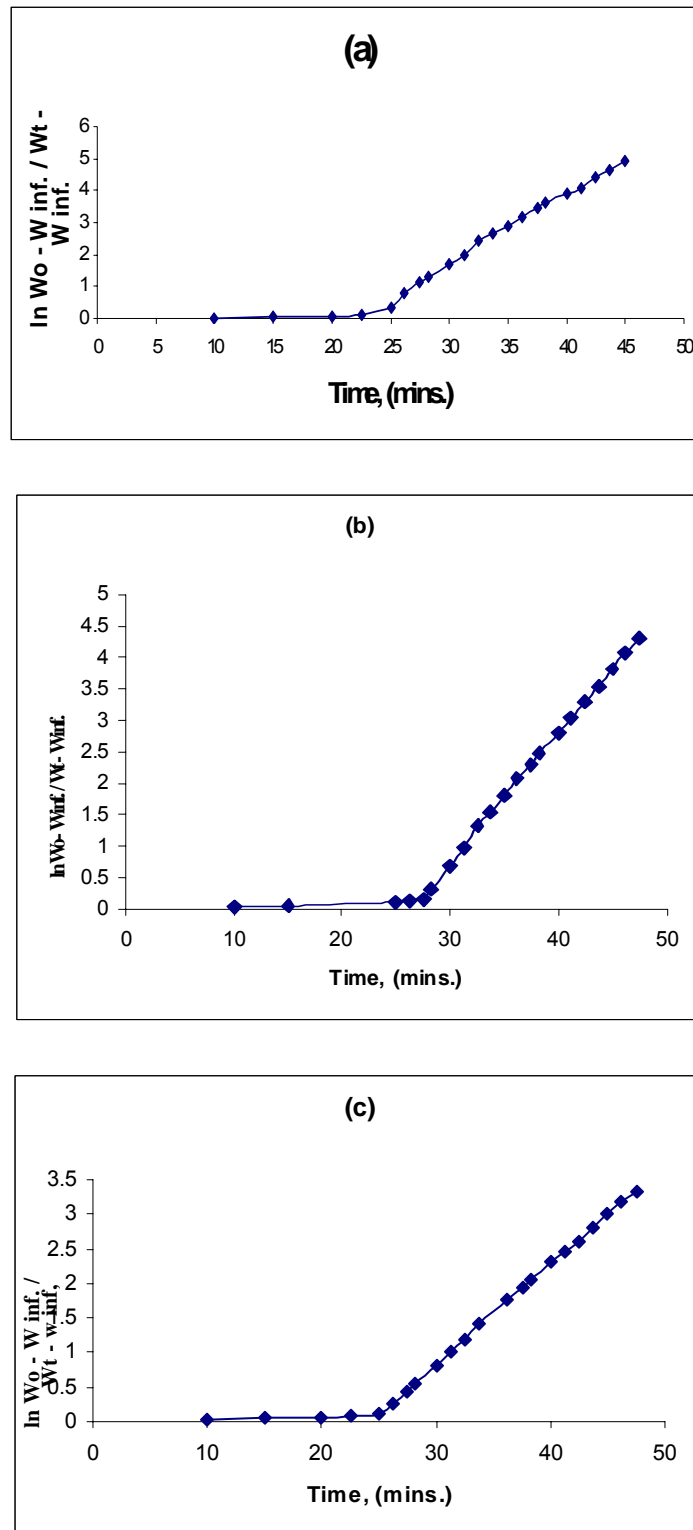


Fig. 3. Relation between $\ln \frac{W_o - W_{inf.}}{W_t - W_{inf.}}$ vs. time (mins) of untreated Cellulose (a), cellulose hydrolyzed with 5 % HCl (b) and cellulose hydrolyzed with 15 % HCl (c)

Scanning Electron Microscopy (SEM)

Figure 4 shows the SEM micrographs of the cotton linters hydrolyzed with 5% and 15% HCl, and unhydrolyzed cotton linters. In this study we examined the microstructures of these samples in order to understand the changes in fiber structure, shape, and particle size by effect of acid concentration.

From part 4a of the figure, the cotton linters fibers resembled their initial condition, while in Fig. 4b it is apparent that shortening and cracking of these fibers had occurred by effect of the acid hydrolysis. Also, Figure 4c shows that more shortening and cracking in fibers occurred, resulting in small particle size, and rod-shaped microcrystalline cellulose had formed. This can be attributed to the effect of extending the hydrolysis of fibers by 15% HCl.

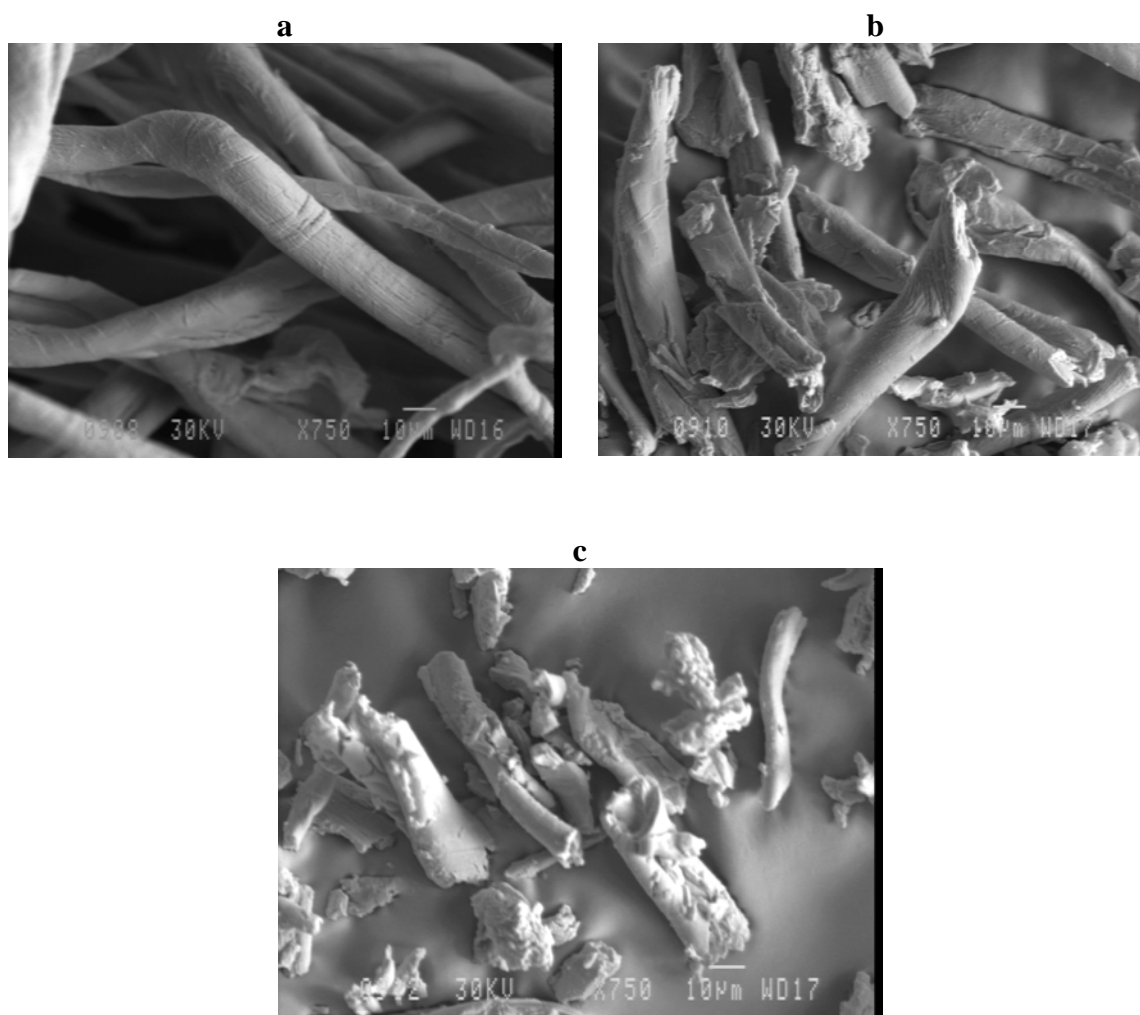


Fig. 4. SEM photomicrograph of the untreated cotton linters magnified 750× (A), hydrolyzed cotton linters with 5% HCl magnified 750×; (B) hydrolyzed cotton linters with 15% HCl magnified 750× (C)

CONCLUSIONS

1. Microcrystalline cellulose (MCC) was prepared by acid hydrolysis of cotton linters with HCl.
2. Acid hydrolysis of cotton linters with 5% produced microcrystalline cellulose with higher yield and higher proportion of crystalline region than hydrolysis with 15% HCl.
3. Hydrolyzed cotton linters with low acid concentration produced MCC with lower major decomposition temperature and weight loss percentage in comparison to the hydrolyzed cotton linters with 15% HCl.
4. MCC produced from hydrolysis with low acid had a higher kinetic energy than linters that were untreated or hydrolyzed with 15% HCl.
5. MCC produced from hydrolysis with low acid concentration is more resistant to degradation and thermal treatment than either that produced from higher acid concentration or untreated sample.

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Article submitted: April 23, 2009; in formatted form for peer review: May 24, 2009; Peer review completed: July 18, 2009; Revised version received and accepted: Aug. 16, 2009; Published: Aug. 28, 2009.