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Evaluation Studies of Hydrogen Bond, Crystallinity and Water Propensity of Acid Treated *Bambusa vulgaris* Cellulose Particles

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ARTICLE INFORMATION

ABSTRACT

Cellulose, the most abundant natural polymer on earth has found its use in different applications. Studies have demonstrated cellulose response to acid and alkali solutions in terms of reduction in polymerization degree, crystallinity and morphological changes. This research focuses on inter and intra hydrogen bonding, crystallinity and water retention strength of cellulose particles exposed to acids. Bamboo particles obtained from bamboo plant was treated with 1 M NaOH for 1 hr. The residue (cellulose) was washed to neutral pH and oven dried at 70 ºC for 4 hrs. Three grams of cellulose particles (CP) was soaked in 1 M each of HCl (HCP) and H_3PO_4 (H3CP) for 1 week. Samples were characterized via Fourier transform infrared spectroscopy (FTIR), X-Ray diffraction (XRD) and differential scanning calorimetry (DSC). Average maximum hydrogen bond energy (EHav) from FTIR was 4.45 KCal for HCP and 4.13 kCal for H3CP. Crystallinity of 55.9, 73 and 78% are calculated for CP, H3CP- and HCP respectively. The water molecule holding capacities from DSC was calculated to be 1.34, 2.30 and 11.30 J/g for CP, H3CP, and HCP. Treatment with acid improves the quality of cellulose as amorphous constituents such as lignin and hemicellulose present in CP are eliminated.

1. INTRODUCTION

Cellulose is a biopolymer used in industries such as textile, paper, food, medicine, biochemical and energy (Chakraborty and Gaikwad, 2012; Sindhu et al., 2014). It is a renewable material and it is ranked the most abundant natural polymer on earth. Cellulose is found in plants where it performs a key role in imparting

mechanical strength to their cell walls as confirmed by Kittle (2012). The molecular bonds existing in its structure is affirmed to be responsible for the mechanical strength, while hydrophobicity of cellulose is attributed to high molecular weight of more than 500.000 Da possessed by its long chains (Wulandari *et al.*, 2016). As a class of structural polysaccharides, its physical properties are dependent on the three OH groups in its structure. A primary OH is situated at C-6 while the two secondary OH groups are positioned at C-2 and C-3 respectively (Figure 1). Cellulose is confirmed to possess two intra molecular hydrogen bonds O (2)H…O (6) and O (3)H…O (5) with one inter molecular bond at O (3)H…O (5) as illustrated in Figure 1. These molecular bonds are responsible for its crystalline form and thermal stability (Ciolacu *et al.*, 2010). Cellulose has been investigated to be of four polymorphs: cellulose I, II, III and IV (Gautam *et al.*, 2010). Types I and II cellulose are the most common and the former is reported to maintain the most appreciable mechanical properties of all (Gautam *et al.*, 2010; Wulandari *et al.*, 2016).
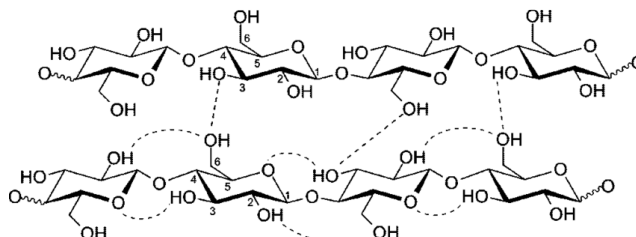

Figure 1: Intra and intermolecular hydrogen bonds in cellulose (Pinkert *et al.*, 2009)

Over the years, researchers have investigated the response of cellulose when exposed majorly to acidic environments. Yamashit and Endo (2004) used acidic (HCl) and basic (NaOH) solutions to study the deterioration behaviour of cellulose acetate (CA) films. The films became opaque and rubbery after immersion in these solutions; they later shrank and finally became brittle when dried. Weight change of CA was observed to be dependent on solution concentration and immersion time with deterioration more pronounced in HCl. Cellulose sourced from middle length cotton fiber was treated with different concentrations of tetraoxosulphate (VI) acid, H_2SO_4 (50-65 wt. %) at room and elevated temperatures (45°C) (Ioelovich, 2013). The choice of this acid was made because of its low cost and the ability to form negatively charged sulfonic groups (SO_3H) that hinders the precipitation of cellulose particles in aqueous solutions during hydrolysis. Treatment with the acids at room temperature enhanced cellulose depolymerization and its solubility was promoted. At elevated temperatures, sulfonic groups in the acid also increased. There was a minor change in cellulose crystallinity between treatment with dilute and concentrated H_2SO_4. X- Ray analysis showed cellulose I polymorph at low concentration while treatment with 65wt. % H_2SO_4 engendered a cellulose II cellulose polymorph. Hydrochloric acid and H_2SO_4 have been used on pure cotton wool cellulose to decipher its structural transformations via scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) (Ioelovich, 2017). Dilute forms of these acids (3 M) enhanced splitting of long cotton fibers. They attributed this to degradation of amorphous domains in the material. High concentrations of these mineral acids (9M) culminated in degradation of amorphous contents and also, there was release of free cellulose nano-crystallites. Further investigation by Ioelovich (2018) claims that cellulose (sourced from bleached kraft pulp) hydrolysis can be hastened at a low temperature and increased concentration of H_2SO_4. Works such as these, however, have explained cellulose response to acid/alkaline solutions as it affects its degree of polymerization and structure. The structural investigations however, have excluded the influence of these aqueous media on cellulose hydrogen bonds coupled with their ctrystalline phases and tendency to interact with water molecules. he current research focuses on inter and intra hydrogen bonding, crystallinity and thermal stability (in relation to dehydration) of bamboo sourced cellulose particles exposed to two different inorganic acids.

2. MATERIALS AND METHODS

2.1. Cellulose Extraction

Bamboo particles of 150 μm were obtained from bamboo plant sourced from Abakaliki, Ebonyi State Nigeria (6.2649 ºN, 8.0137 ºE). The particles were treated in 1 M NaOH for 1hr to dissolve lignin and hemicellulose from the biomass. The residue (cellulose) was washed with distilled water to neutral pH and oven dried at 70 ºC for 4hrs to remove other moisture contents. Three grams of cellulose particles (CP) was soaked in 1 M of hydrochloric acid (HCl) and tetraoxophosphate (V) acid (H_3PO_4) for 1 week. At the end of this period, CP samples were characterized. In this study, the CP soaked in HCl and H_3PO_4 were designated as HCP and H3CP respectively.

2.2. Characterization Tests

2.2.1. Fourier transform infrared spectroscopy (FTIR)

Ten milligrams each of CP, HCP and H3CP were characterized for functional group detection with the use of a Nicolet 6700M spectrometer. Results were processed between 800–3600 cm^{-1} in absorbance mode. Adopting works of Ciolacu *et al.*, (2010), the hydrogen bond energy E_H (kCal) in CP, HCP and H3CP were calculated using Equation (1). This was done by resolving and improving the absorption broad bands between 3600 and 3000 cm^{-1} by their deconvolution from a background scattering using a Gaussian function curve-fitting analysis with an $r^2 > 0.99$.

$$E_H \text{ (kCal)} = [1/k \; \times \; (V_o - V)/V_o] \tag{1}$$

V_o is the frequency of free OH groups at 3600 cm^{-1}; V is the frequency of the bonded OH groups and k = 1.68 x 10^{-2} kcal^{-1}.

2.2.2. X-Ray diffraction (XRD)

Cellulose particles were analysed for their crystallinity after immersion in the acids with the use of a PANanalytical XRD device operated at 40 kV and 40 mA. The height ratio was used in calculating the crystallinity of samples from the diffractogram using Equation (2) (Juarez-de la Rosa *et al.*, 2012).

$$X_c \text{ (\%)} = [I_c /(I_c + Ia)] \times 100 \tag{2}$$

I_c and I_a represent the intensities of the crystalline and amorphous regions respectively.

2.2.3. Differential scanning calorimetry (DSC)

A Mettler Toledo DSC equipment was used in heating up CP, HCP and H3CP from 0 to 160 ºC at the rate of 10 ºC/min. Temperatures of major reactions and energies associated with them (in terms of enthalpy change (ΔH), were obtained from the DSC results, which were used as a measure of their thermal stabilities.

3. RESULTS AND DISCUSSION

3.1. FTIR Results

Figure 2a shows the spectra of CP, HCP and H3CP between 3600 – 2600 cm^{-1}. All samples' spectra showed similar patterns but with different intensities indicating CP's varying response to the acids used in this study. The wavenumbers 3329, 3308 and 3267 cm^{-1} represent O-H stretching vibrations while that occurring at 2884 cm^{-1} is indicative of CH stretching (Liew *et al.*, 2015; Abdul Rahman *et al.*, 2017). It is observed that the spectrum for CP is the broadest with the least absorbance of all samples. This is as a result of the presence of some amorphous constituents such as lignin and hemicellulose in the untreated particles which are present in ligtnocellulosic materials (Gbenebor *et al.*, 2020). Narrow peaks were recorded for H3CP and HCP, indicating that the acids were able to further attack amorphous constituents in the CP. All cellulose samples display characteristics of cellulose I type. The two peaks displayed by HCP reflect the orderliness of cellulose structure in preventing water absorption. Spectra between 1800 – 800 cm^{-1} (Figure 2b) has OH stretching of absorbed water on 1653 cm^{-1}while CH_2CH_3 vibrations occur on 1454 cm^{-1}. Vibration on 1567 and 1303 cm^{-}

[1] represent C–H stretching in cellulose; C-O-C vibration in cellulose is absorbed on 1156 and 1109 cm^{-1} while at 1045 and 1022 cm^{-1}, C-O and C-C vibrations in glycosydic linkage are absorbed. Deformation of C-H in cellulose is absorbed on 887 cm^{-1} (Liew *et al.*, 2015).

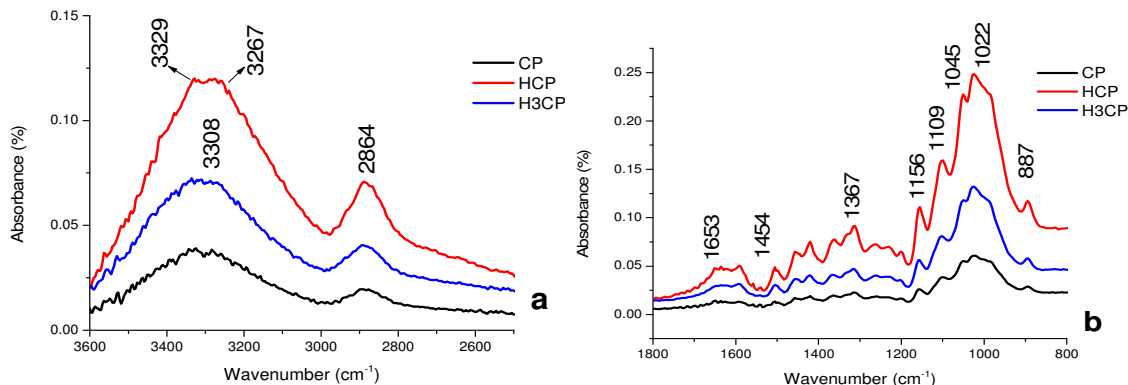Figure 2: FTIR spectra between (a) 3600 – 2600 cm^{-1} and (b) between 1600 – 800 cm^{-1} For CP, H3CP and HCP

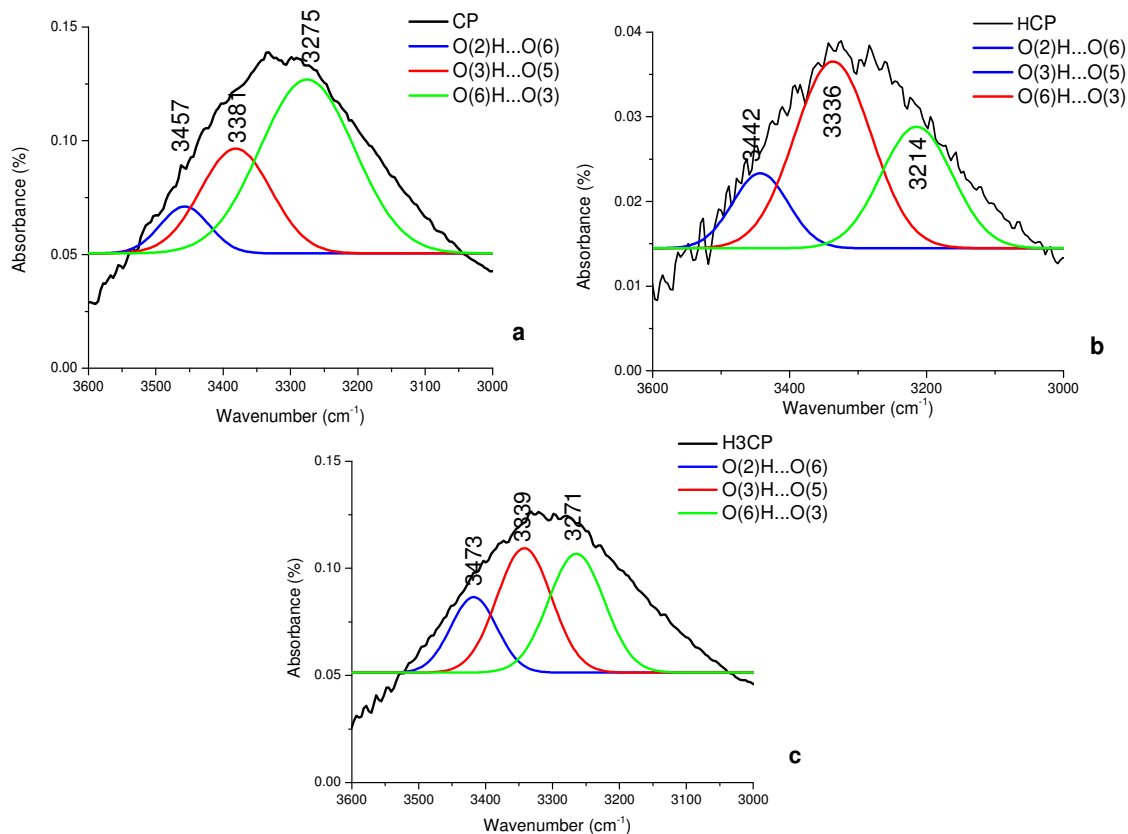Figure 3: OH, bonds present in (a) CP (b) HCP and (c) H3CP between 3600-3000 cm^{-1}

Hydrogen bonds in CP comprises intra molecular H bonds at 3457 cm^{-1} for O (2)H…O (6) and 3381 cm^{-1} for O (3)H…O (5) as shown in Figure 3a. The intermolecular H bond O (6)H…O (3) is absorbed on 3275 cm^{-1}. These bonds are responsible for the mechanical strength and polymeric chain formation of cellulose.

Table 1 shows that the intermolecular O (6)H…O (3) in CP possesses the highest magnitude of hydrogen bond energy (EH) of the three bonds (5.37 kCal). Exposure of CP to the acidic media further increases cellulose average EH, an indication of hydrogen bond strengthening via removal of amorphous and other volatile constituents remaining in CP. There exists 17.8% increase in CPs average bond energy (EHav) as 4.45 kCal was calculated on exposure to HCl (Figure 3b). The O (2)H…O (6) and O (3)H…O (5) bonds lie on 3442 and 33336 cm^{-1}while O (3)H…O (5) is absorbed on 3214 cm^{-1}. Tetraoxosulphate (V) acid action on cellulose (H3CP) results in the shifting of O (2)H…O (6), O (3)H…O (5) and O (3)H…O (5) bond bands to 3473, 3339 and 3271 cm^{-1} for the intra and intermolecular bonds respectively (Figure 3c) with 7.2% reduction in in EHav when compared to HCP.

Table 1: FTIR absorption band assignment to the hydrogen bond (3600-3000 cm^{-1}) in cellulose

| Samples | O (2)H…O (6) | | | O (3)H…O (5) | | | O (6)H…O (3) | | | |
	cm^{-1}	Amount (%)	EH (KCal)	cm^{-1}	Amount (%)	EH (kCal)	cm^{-1}	Amount (%)	EHav (kCal)	EHav (KCal)
HCP	3442	15.4	2.61	3336	52.4	4.37	3214	32.2	6.38	4.45
H3CP	3473	6.4	2.10	3339	41.8	4.31	3271	51.8	5.99	4.13
CP	3457	8.8	2.36	3381	28.3	3.62	3275	62.9	5.37	3.78

3.2. XRD Results

Diffraction patterns of CP shown in Figure 4 reveals a major peak at 2θ = 22.2° (200) with a Crl of 55.9%. Peaks at 2θ = 14.7°, 16.8° and 22.1° corresponding to (1Ī0), (110) and (200) planes are obtained on reaction with HCl i.e., HCP. Reaction of CP with H$_3$PO$_4$ displays cellulose III polymorph as it shows major peaks at (110) and (200) with a minor peak at 2θ = 7.69°. Huntley et al. (2015) confirmed two minor peaks on the XRD of wheat straw at 2θ = 7.5 and 11.7° and they characterized this to be typical cellulose III polymorph. Cellulose chain splitting could have been responsible for the part transformation. Thus, cellulose I and III polymorphic forms of cellulose can be sourced from bamboo particles with the use of H$_3$PO$_4$. Crystallinity index attained a maximum value of 78.1% for HCP and 73% for H3CP.
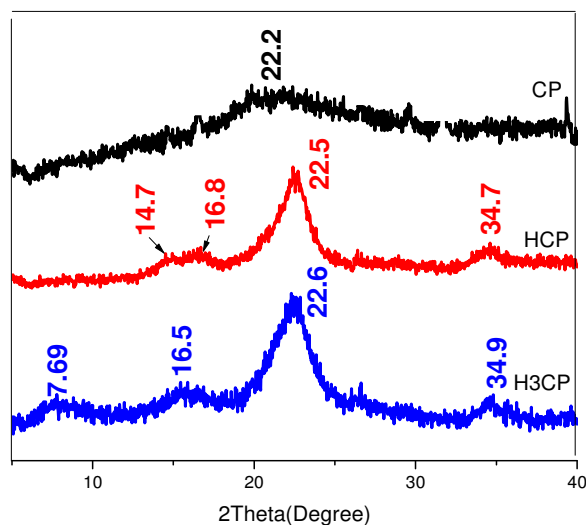

Figure 4: XRD of CP, HCP and H3CP

3.3. DSC Results

The DSC plots for CP, H3CP and HCP is displayed in Figure 5. There exist different thermal intensities and temperatures at 112, 119 and 148 °C for treated and untreated CP respectively. These thermal events are characteristics of hydrophilic nature of cellulose, which is a function of the OH groups in its structure as explained by the FTIR spectra (see Figure 2). At 112 °C, CP gets dehydrated while H3CP loses its water molecules at 119 °C. It is observed that HCP gives up its moisture at 148 °C. The difference in their water molecule holding capacities is further evidenced in the enthalpies related to the biopolymers, which were calculated to be 1.34, 2.30 and 11.30 J/g for CP, H3CP, and HCP. Findings from this study have shown that the crystalline nature of HCP is responsible for the greatest magnitude of energy required in eliminating water molecules from cellulose.
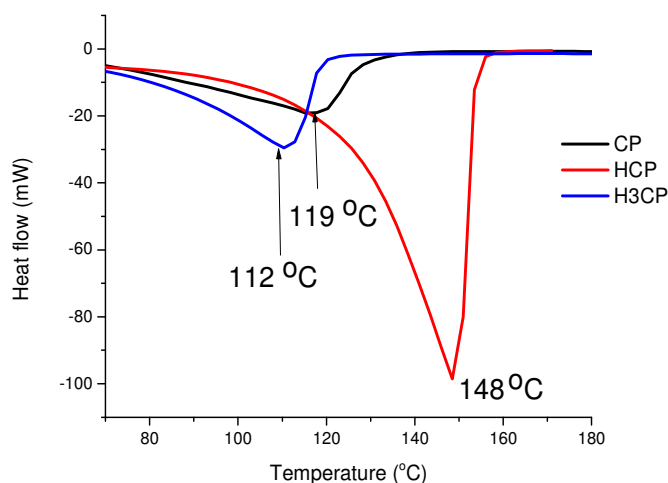

Figure 5: DSC of CP, HCP and H3CP

4. CONCLUSION

Elimination of amorphous phases such as lignin and hemicellulose will enhance the hydrophobicity of cellulose as they will be more resistant to aqueous solution penetrations when compared to CP. The maximum EHav of 4.45 kCal possessed by HCP which is ≈ 18 and 8% higher than that of H3CP and CP further justifies the strengthening effect imparted by elimination of amorphous molecules. All cellulose samples from bamboo display characteristics of CI type. In addition, a combination of cellulose I and III polymorphic forms was achieved with the use of H_3PO_4. This transformation could have occurred as a result of chain splitting of CP during reaction. Crystallinity index has a maximum value of 78.1% in HCP and 73% in H3CP. (The crystalline nature of the cellulose variants is responsible for their water retention capacity stabilities at temperatures between 100 – 1150 °C. At 148 °C, 11.3 J/g is required for the elimination of water molecules from HCP's structure; 119 °C and 2.30 J/g are need for H3CP while 112 °C is exhibited by CP at 1.34 J/g. Treatment with acid improves the quality of cellulose as amorphous constituents such as lignin and hemicellulose still present in CP are eliminated.

5. ACKNOWLEDGMENT

6. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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