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EFFECT OF ACETYLATION ON THE PORE MATRIX AND PHYSICOCHEMICAL PROPERTIES OF LIGNOCELLULOSIC FIBERS

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Abstract: The recent resurgence of interest in the use of fibers from agro – waste as reinforcement and oil sorption materials in the polymer and oil spill cleanup industries respectively, has directed focus on chemical modification of lignocellulosic fibers. This research studied the effect of acetylation on the physicochemical properties of lignocellulosic samples. Oil palm empty fruit bunch (OPEFB), pride of Barbados Pods (POBP) and cocoa pod (CP) samples were acetylated at 70°C for 90 min, in the presence of n–bromo succinimide (NBS) catalyst using a solvent free method. The modified (acetylated) and unmodified (unacetylated) samples were further characterized using scanning electron microscope (SEM) and X–ray diffractometer (XRD) analysis. The results showed that acetylation did not affect the ash content significantly but reduced the moisture content and bulk densities (compacted and uncompacted) of the lignocellulosic samples while the XRD analysis showed that acetylation reduced the crystallinity index of the samples. Pore analysis using SEM showed that the lignocellulosic samples are made up of pores of various sizes and majority of the pores are of small size range with few medium and large pore sizes. Results showed that acetylation affected the various sizes of the pores (pore matrix) differently and this consequently affected the porosity of the lignocellulosic samples. Thus, acetylation improved the composite and oil sorption properties of lignocellulosic materials.

Keywords: Pore analysis, acetylation, physicochemical properties, lignocellulosic

Introduction

Lignocellulosics are generally cellulose fibers consisting of helically wound cellulose microfibrils in an amorphous matrix of lignin and hemicellulose. The properties of these fibers are strongly influenced by many factors, particularly chemical composition and internal fiber structure, which differ between different parts of a plant as well as between different plants (Thomas *et al*., 1996).

Cellulose fibers present many advantages compared to synthetic fibers which make them attractive as reinforcements in composite materials and sorbents for hydrocarbons in aqueous mediums. Cellulose fibers are non-toxic, easy to handle and present no health problems like synthetic fibers (glass fibers) that can cause skin irritations and respiratory diseases when the fibrous dust is inhaled (Supri and Lim, 2009). They offer a high ability for surface modification, they are economical, require low amounts of energy for processing, and are biodegradable (Adebajo and Frost, 2004). In terms of socio – economic issues, the use of cellulose fibers as source of raw materials is beneficial because it generates economic development opportunity for non-food farm products in rural areas. Cellulose fibers come from lignocellulosics (agro – wastes) which are abundant and renewable resources at low cost, and which also ensures continuous fiber supply as cost effective material for reinforcements in plastic and oil spill cleanup applications. Despite the low strength of cellulose fibers, they can lead to composites with high specific properties because of their low densities (Sanadi *et al*., 1994).

One of the primary drawbacks of using cellulose fibers is their limited thermal stability with noticeable degradation occurring as the melt processing temperature approaches 200°C (Pereira *et al*., 1997). Another major drawback of using cellulose fibers as reinforcing agent is the high moisture absorption capacity of the fibers due to hydrogen bonding of water molecules to the hydroxyl groups within the fiber cell wall. This leads to a moisture build-up in the fiber cell wall (fiber swelling) and also in the fiber – matrix interface. This is responsible for changes in the dimensions of cellulose-based composites and the preferential absorption of water in oil – water medium. Other than dimensional stability, the hygroscopic and hydrophilic nature of cellulose fibers also influences the composites' processability. Poor compatibility with and dispersability of cellulose fiber in hydrophobic thermoplastics leads to poor wetting and interfacial bonding between the fibers and the matrix resulting in composites with poor mechanical properties (George *et al.*, 1998). The tendency of cellulose fibers to absorb moisture causes off-gassing (void formation) during compounding. This results in a molded article with a microstructure having variable porosity and resembling that of high-density foam. The pores formed will act as stress concentration points which then lead to an early failure of the composite during loading (Thomas *et al*., 1996).

Lignocellulosic fibers degrade easily when exposed to nature. Nature builds lignocellulosic resources from carbon dioxide and water, and it has all the tools to recycle them back to the starting chemicals. Possible ways of degradation include biological, thermal, aqueous, photochemical, chemical, and mechanical means of degradation. In order to produce cellulose fiber-based composites with a long service life, the degradation processes caused by nature need to be retarded (Rowell *et al*., 1994).

One way of preventing or slowing down the natural degradation process is by modifying the cell wall chemistry of the lignocellulosic fibers which is responsible for many of its properties. This can be accomplished by surface chemical modification such as plasma activation, graft polymerization with vinyl monomers, and acetylation using acetic anhydride to produce an acetylated material. However, these will increase the fiber cost (Azeh *et al*., 2012).

This research investigates how acetylation affects the pore matrices and physicochemical properties of selected lignocellulosic fibers.

Materials and Methods

Sample collection and preparation

The agro – wastes samples; oil palm empty fruit bunch (OPEFB) and cocoa pods (CP) were obtained from local farms at Anambra State while pride of barbados pods (POBP) was collected from the premises of National Research

Institute for Chemical Technology (NARICT), Zaria. The samples were cut and ground in a mortar. Then, thoroughly washed with distilled water to remove foreign materials, and water soluble components. This allowed the samples to maintain balance. The washed samples were allowed to air dried properly for 24 h and then oven dried to a constant weight at 65 ^oC for 48 h.

After drying, the materials were sieved with laboratory sieves to obtain homogenous particle sizes using the BS410/1986 laboratory test sieve. A mechanical sieve shaker was used to separate the samples into the desired particle size (i.e., 425 – 625 µm).

Acetylation of the lignocellulosic samples

The acetylation of the lignocellulosic samples under mild conditions, in the presence of N – bromosuccinimide (NBS), using acetic anhydride was carried out in a solvent free system described by Sun *et al.* (2004) and Onwuka *et al.* (2016).

A portion (3 g) of sample was placed in a 250 mL conical flask containing 60 mL of acetic anhydride and 0.6 g (1% of the solvent) N – bromosuccinimide (NBS). Acetylation was done at constant temperature of 70^{o}C for 90 min, in a temperature controlled water bath. The flask was removed from the bath and the hot reagent was decanted. The sample was thoroughly washed with ethanol and acetone to remove unreacted acetic anhydride and acetic acid by – product. The products were oven dried at 60^{o}C for 16 h, and later cooled and stored in a plastic container for physicochemical characterization.

Physicochemical characterization of the lignocellulosic samples

Proximate analysis and physical characteristics of the acetylated and unacetylated samples were determined as follows;

Moisture content determination

A 2 g portion of the sample was measured into a wash glass and placed in the oven for 24 h at 105^{o}C. After 24 h, the oven dried sample was reweighed and the moisture content (MC) determined using the expression

$MC = [(W_1 – W_2)/W_1] \times 100$ (1)

Where MC is the moisture content; W_1 is the initial weight of the sample; W_2 is the new weight after drying (ASTM, 1994).

Ash content determination

Ash content was determined using the methods employed by Dara (1991) and Aloko and Adebayo (2007). Dried sample (2 g) was placed in a pre – weighed porcelain crucible and transferred into a preheated muffle furnace set at a temperature of 600^{o}C for 1 h after which the crucible and its content were transferred to a dessicator and allowed to cool. The crucible and its content were reweighed and the new weight noted. The percentage ash content was calculated using the expression

$AC (\%) = (W_a/W_o) \times 100$ (2)

Where AC is the ash content in percentage; W_a is the weight of ash after cooling and W_o is the original weight of dried sample.

True density or particle density determination

A portion (25 g) of the sample was accurately weighed into a 100 mL graduated cylinder, and the volume measurement of the sample (V) was recorded. Distilled water was carefully poured into the cylinder to the level of the sample. The true density was calculated as follows:

True or Particle Density = W/V (3)

Where W is the weight of the sample and water in the measuring cylinder and V is the volume of the sample (ASTM, 1994).

Bulk and tapped density determination

A portion (25 g) of the sample was accurately weighed into a 100 mL graduated cylinder. The cylinder was stoppered and the bulk volume (V_o) of the weighed sample was recorded. For tapped or compacted density, the cylinder was tapped on a hard surface to a constant volume (until no more settling of the material occurred). The final constant volume (V_1) was noted to be the tapped volume.

The bulk (uncompacted) D_{bulk} and tapped (compacted) D_{tap} densities were calculated as follows:

$D_{bulk} = W/V_o$ (4a)

$D_{tap} = W/V_1$ (4b)

Where W is the weight of the sample (ASTM, 1994).

Porosity determination

The porosity of the sample was calculated using the calculated bulk density at Equation 4a and calculated particle density at Equation 3. The expression for calculating porosity is

Porosity = 1 - (BD/PD) (5)

Where BD is the bulk density while PD is the particle density (ASTM, 1994)

Swellability (S) and anti-swelling efficiency (ASE) determination

The anti – swelling efficiency was determined after 5 g each, of the samples (unacetylated and acetylated) were soaked separately in a 250 mL beaker containing 100 mL distilled water. The beaker and its contents were kept for 5 days at room temperature and the distilled water was replaced daily. The volumetric swelling coefficient or swellability was calculated using the expression

$S (\%) = [(V_{wet}-V_{dry})/V_{dry}] \times 100$ (6)

Where V_{wet} is the volume of water saturated sample and V_{dry} is the volume of dried sample

The percentage of anti – swelling efficiency (ASE) was calculated as follows:

$ASE (\%) = [(S_o-S)/S_o] \times 100$ (7)

Where S_o is the volumetric swelling of the unmodified (unacetylated) sample and S is the volumetric swelling of the modified (acetylated) sample (Temiz *et al.*, 2006)

X–ray diffraction analysis

X-ray diffraction analysis (XRD) of the sample was performed with Empyrean diffractometer. The oven dried sample was finely ground, homogenized, and sieved to pass through the 75 microns mesh. A representative portion of the powdered sample was then prepared using the sample preparation block and compressed in the flat sample holder to create a flat, smooth surface that was later mounted on the sample stage in the XRD cabinet.

The sample was analysed using the reflection-transmission spinner stage using the Theta-Theta settings. The 2Θ starting position was 0.00483 and ends at 75.000 with a 2Θ step of 0.026 at 3.57 sec per step. Tube current was 40 mA and the tention was 45 VA. Fixed divergent slit size of 1^0 was used and the goniometer radius was 240 mm. The crystallinity index was calculated from the equation (Segal *et al.*, 1959):

$$CrI = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \qquad (8)$$

Where CrI indicates the relative degree of crystallinity, I_{002} is the maximum intensity (in arbitrary units) of the 002 lattice diffraction at $2\theta = 22°$, and I_{am} is the intensity of diffraction in the same units at $2\theta = 18°$

Oil sorption

The acetylated samples only were subjected to crude oil sorption test using method described by Onwuka *et al.* (2016). To 100 mL of distilled water in a 250 mL beaker, 2.5 g of crude oil was added. A 0.5 g portion of the sample was added into the mixture in the beaker and left unperturbed for 10 min. Then, the sample was removed using sieving net and left to drain by hanging the net over the beaker in an oven for 4 h at 60^{o}C. The drained sample was stored for pore analysis.

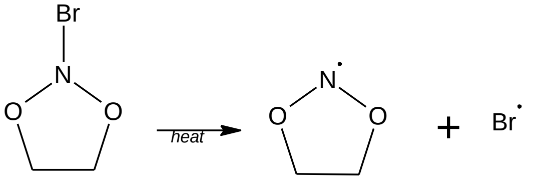
Pore analysis

A Phenom World model of SEM machine was used for pore analysis. About 20 mg of the oven dried sample was sputter coated with a gold layer in a sputter machine (quantum sputter) for a 90 sec. The SEM machine was allowed to stabilize for 120 sec before setting the parameters to be used. Imaging of the sample was properly done at 15 kV, pressure at 0.003 Pa and set at 1000 magnification. Phenom suite software was used in the measurement of pores present in the sample image used.

Proposed mechanism of acetylating the lignocellulosic samples

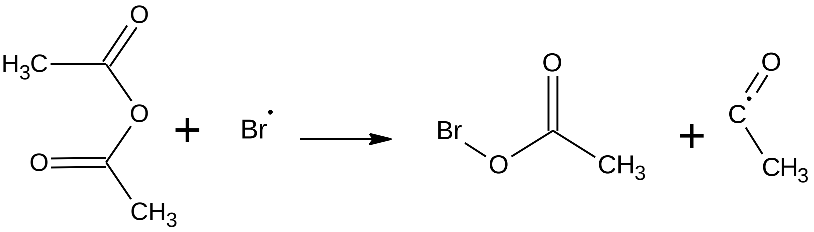
Acetylation of lignocellulosic sample is a three stage mechanism that involves the replacement of the hydrogen atom of the reactive hydroxyl (OH) site in the surface of lignocellulosic with an acetyl group, resulting in the formation of acetates in the lignocellulose substrate. The mechanism is one of free radical reactions.

The first step involves the reaction of NBS with acetic anhydride to produce a strong acetylating agent. The splitting of the hemolytic cleavage of the N – Br bond generates a Br radical, which removes an acetate group from the acetic anhydride.



(9)

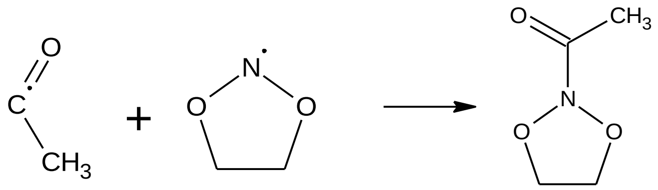
NBS **Succinimide Radical** **Bromine Radical**



Acetic Anhydride **Bromine Radical** **Bromine Acetate** **Acetyl Radical**

(10)

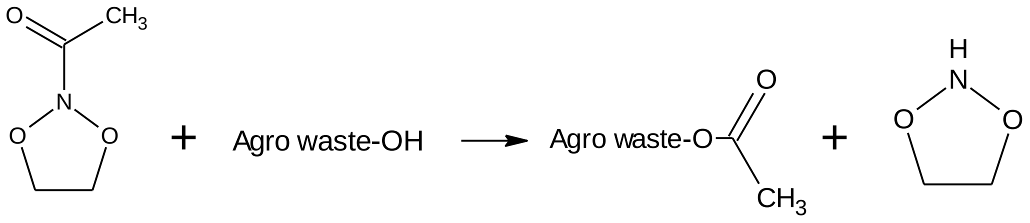
The acyl carbon center of the acetyl radical forms acetyl succinimide, which is a very reactive and unstable acetylating agent, with the nitrogen radical of the succinimide



Acetyl Radical **Succinimide Radical** **Acetyl Succinimide**

(11)

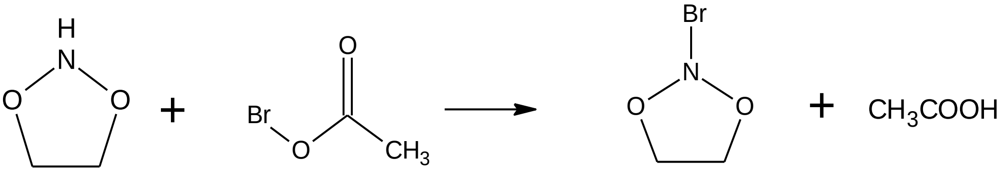
The second stage involves a nucleophilic attack on the acyl carbon center of the acetylating agent by a lone pair of the hydroxyl group followed by the reduction of the acetylating agent to succinimide and thus generating the agro-waste (sample) acetates.



Acetyl Succinimide **Agro-waste Cellulose** **Agro-waste Acetate** **Succinimide**

(12)

In the third stage, the succinimide produced reacts with the brominated acetate group, produced in 10, resulting in the loss of acetic acid and the regeneration of the N – bromosuccinimide (NBS) catalyst.



Succinimide **Bromine Acetate** **NBS** **Acetic acid**

(13)

The acetates are then washed with excess of acetone and ethanol to remove the by – products namely, acetic acid, NBS and unreacted acetic anhydride (Nwankwere, 2010; Onwuka, 2015).

Results and Discussion

Physicochemical analysis

The results of the proximate analysis and physical properties of the unmodified (unacetylated) and modified (acetylated) samples are presented in Table 1. The Table showed that after acetylation, there was a decrease in the moisture contents, bulk (compacted and uncompacted) densities and swellability coefficients of all the samples as well as the particle density and porosity of OPEFB and CP. It was also observed that there is no significant difference in the ash contents of the unmodified and modified samples.

The experimental data in Table 1 revealed that the moisture contents of the unmodified samples were significantly higher than those of the modified samples. The moisture contents decreased from 8.66 to 7.93%, 7.07 to 6.79%, and 10.00 to 6.13% for OPEFB, POBP and CP respectively. This is as a result of reduction in hydrophilic nature of the material by substitution of the hydroxyl groups in the unmodified samples with acetyl groups. This implies that the dispersability of the lignocellulosic as reinforcing agent in thermoplastic has been improved by acetylation. The amount of moisture absorption in the cellulose fibers can be dramatically reduced through chemical modification, such as acetylation, of some of the hydroxyl groups present in the fibers (Gatenholm *et al*., 1991; Raj *et al*., 1995; Rana *et al*., 1997).

The data also showed that there is no significant difference in the ash content of the unmodified and modified samples. This implies that acetylation did not affect the inorganic constituents of the samples. Thompson *et al*. (2010) reported similar findings for rice husk.

There was a decrease in the bulk (compacted and uncompacted) densities of all the samples as well as the particle density and porosity of OPEFB and CP. Most researches on acetylation reported increase in particle and bulk densities after acetylation (Thompson *et al*., 2010) but in this study, acetylation caused decrease in bulk (compacted and uncompacted) densities of all the lignocellulosic samples as well as particle densities of OPEFB and CP. This could be due to decrease in degree of crystallinity of the modified samples compared to unmodified since substitution of hydroxyl group by acetyl groups weakens the inter – and intra – molecular hydrogen bonds (Hu *et al*., 2011). This results in a more amorphous structure whose molecules are loosely bound, thus, reducing its density as compared to its former structure which is a closely packed molecules with stronger inter – molecular hydrogen bonds.

This decrease in densities (bulk and particle densities) could also be attributed to the removal of surface wax, hemicellulose and lignin during acetylation which resulted in the appearance of a rough surface after acetylation (Wang *et al*., 2012; Onwuka *et al*., 2016). Thus, increase in particle density of POBP after acetylation could be because it contains less amount of these components (surface wax, hemicellulose and lignin) as such substitution is carried out directly at the cellulose – OH groups which makes the impact of the bulkiness of the acetyl groups attached felt. Ray (1953) in his study on the influence of lignin content on the mechanical behavior of jute, reported a gradual decrease in both the strength and stiffness of the fiber with lignin removal. The extensibility of the fiber was also found to follow the same trend. Similar, findings was reported by Collier *et al*. (1997) on sugar cane fibers.

Acetylation of these lignocellulosics was found to improve some of the physical properties of the modified samples. The lower porosity and swellability values of modified samples compared to unmodified samples, makes them better sorbents for oil retention (oil spill application) as swellability influences competition between the oil and water for sorption sites in the lignocellulosics (Thompson *et al*., 2010). This also indicates that the water retaining ability of unmodified samples were reduced by acetylation. However, it was observed that acetylation increases porosity of the modified POBPs sample. This further suggests that acetylation supports sorption because sorption depends on pore size. However, in order to further explain why the acetylation reduces the porosity of OPEFB and CP, pore analysis was carried out and will be discussed in the next section.

The dimensional stability expressed as anti – shrink efficiency (ASE) of acetylated samples as obtained for some of the acetylated samples are given in Table 1. ASE cannot be determined for unacetylated samples because the ASE is a factor of the swelling weight of the unacetylated sample. According to Mohebby and Hadjihassani (2008), when wood is acetylated, it is far less susceptible to shrinking and swelling in the presence of varying atmospheric conditions. Any increase in the weight percent gain (WPG) increases the moisture sorption and decreases the water repellence in the fibers.

Table 1: Physicochemical parameters of the unmodified (unacetylated) and modified (acetylated) samples

	Unmodified OPEFB	**Modified OPEFB**	**Unmodified POBP**	**Modified POBP**	**Unmodified CP**	**Modified CP**
Moisture content (%)	8.66±0.20	7.93±0.04	7.07±0.01	6.79±0.01	10.00±0.40	6.13±0.01
Ash content (%)	7.84±0.30	7.86±0.10	2.87±0.40	2.82±0.20	9.29±0.60	9.31±0.80
Particle or True Density (g/cm^3)	1.130±0.20	1.079±0.04	0.545±0.009	0.884±0.02	1.808±0.30	1.463±0.06
Bulk Density (Uncompacted) (g/cm^3)	0.195±0.00	0.173±0.00	0.098±0.00	0.095±0.01	0.315±0.01	0.275±0.00
Bulk Density (Compacted) (g/cm^3)	0.241±0.00	0.219±0.01	0.114±0.01	0.113±0.01	0.373±0.00	0.344±0.01
Porosity	0.811±0.02	0.797±0.01	0.790±0.00	0.872±0.03	0.793±0.00	0.764±0.07
Swellability Coefficient (%)	23.529±4.00	10.526±2.20	5.600±0.70	5.500±0.50	81.818±6.00	41.667±3.00
ASE (%)	–	25.720±0.36	–	38.26±0.06	–	31.08±0.90

The results in Table 1 showed that swellability of OPEFB, POBP and CP decreased from 23.529 to 10.526%, 5.60 to 5.50% and 81.818 to 41.667%, respectively. This reduction is an evidence of improved hydrophobicity. The reduction in swellability was further evaluated by the anti – shrinking efficiency (ASE) of modified OPEFB, POBP and CP which was found to be 25.72, 38.26, and 31.08%, respectively. The bulk of the research into chemical modification has been focused on improving dimensional stability (Ĉipinytē, 2000). The changes in the physical properties of acetylated samples are evidence of successful acetylation.

X–ray diffraction (XRD) analysis

In order to assess the influence of the modification on the samples crystallinity, x – ray diffraction (XRD) analysis was applied. The XRD patterns of unmodified and modified lignocellulosic material are presented in Figs. 1 – 3 while

Table 2 shows the calculated values of crystallinity index of the samples (unmodified and modified). Figs. 1 – 3 showed broad or diffused peaks appearing at 16°, 22° and 34° in the XRD patterns of all unmodified samples. It was reported that XRD pattern with diffused peak at 22° corresponds to the presence of amorphous silica (Cheng *et al*., 2011). This is further supported by high silica content in OPEFB, and CP ash reported by Udoetok (2012) and Ajayi *et al*. (2007), respectively.

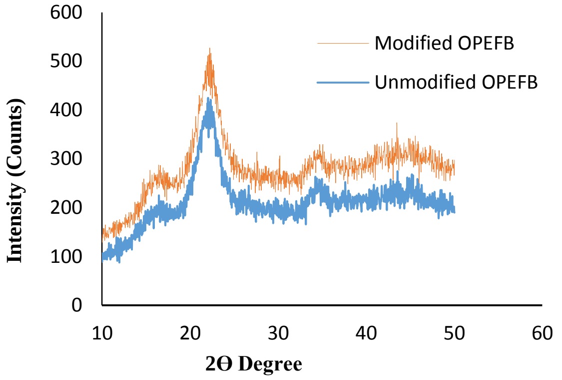


Fig. 1: XRD pattern for unmodified (unacetylated) and modified (acetylated) OPEFB

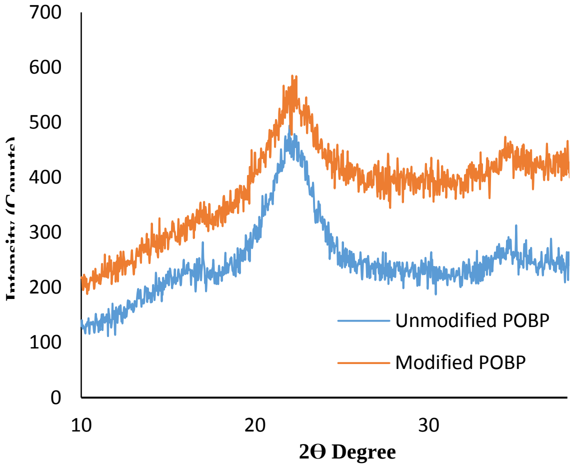


Fig. 2: XRD pattern for unmodified (unacetylated) and modified (acetylated) POBP

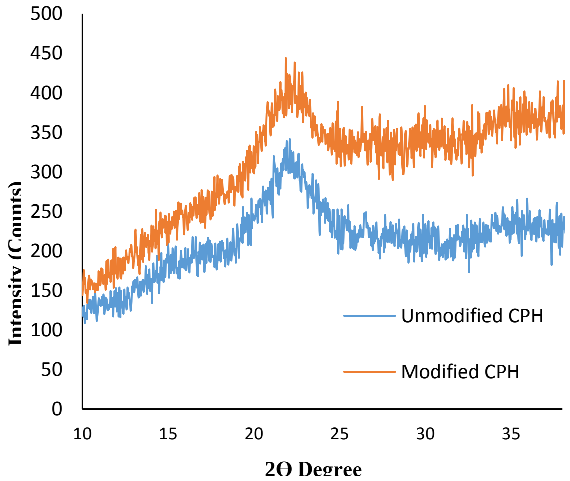


Fig. 3: XRD pattern for unmodified (unacetylated) and modified (acetylated) CP

Table 2: Comparison of CrI values of unmodified (unacetylated) and modified (acetylated) samples

Sample	I_{002}	I_{am}	CrI
Unmodified OPEFB	424.9	186.1	56.2
Modified OPEFB	527.2	242.2	**54.1***
Unmodified POBP	493.2	222.4	54.9
Modified POBP	585.1	336.6	**42.5***
Unmodified CP	341.5	188.9	44.7
Modified CP	438.2	264.8	**39.6***

* is the crystallinity index of modified samples

It was observed from Table 2, that the crystallinity index of all modified samples were lower than that of unmodified. The intensity peaks were reduced significantly in the crystalline patterns of modified samples. This indicates that the structure of the unmodified samples was transformed to an amorphous structure after modification (acetylation) as a result of degradation of crystalline region during acetylation process.

The major part of cellulose is in crystalline form (about two – thirds) due to intra and intermolecular hydrogen bonding of hydroxyl groups (Wang *et al*., 2012). These crystallites mainly have a hydrogen bonding with the hydroxyl group and are attacked by acetic anhydride to form acetylated cellulose in the amorphous structure. The substitution of an acetyl group for a hydroxyl group reduces the density of hydrogen bonding because an acetyl group offers a more bulky branch (a lower ability to form hydrogen bonding) than a hydroxyl group (Yui *et al.*, 2007).

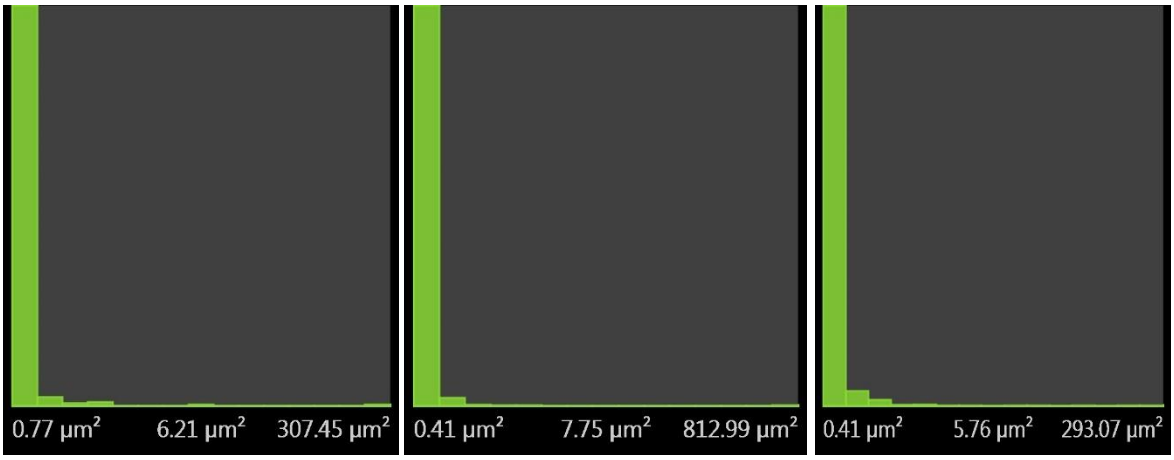
This is an evidence of successful acetylation of the samples and confirms reports by other researchers (Kosaka *et al*., 2005; Tserki *et al*., 2005; Chung *et al.*, 2011) that acetylation of cellulose materials often causes decrease in crystallinity.

Pore analysis

The unacetylated, acetylated and the crude oil sorbed acetylated OPEFB and CP samples were subjected to pore analysis since that of POBPs have been reported in our previous work by Onwuka *et al.* (2016).

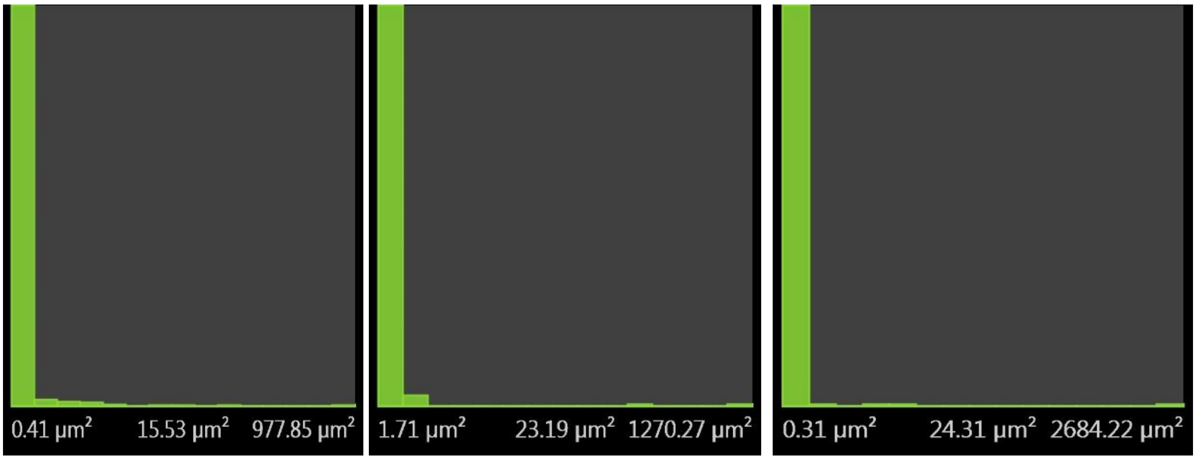
Figures 4a–c and 5a-c showed that various pore sizes were present in the samples (OPEFB and CP) and they were categorized into three different average size ranges. The majority of the pores are of small average size range while the medium and large average pore size ranges are present in few amounts. Fig. 4a-c showed that acetylation of OPEFB significantly reduced the average size of the small pores from 0.77 (Fig. 4a) to 0.41 μm^2 (Fig. 4b) while the average size of the medium and large pores were increased significantly after acetylation. The reduction in the average size of the small pores could be attributed to the opening up of the medium size pores by acetylation (Onwuka *et al*., 2016). However, the reduction in the size of the small pores which are mostly present compared to other pore size range, may have resulted to the reduction in the overall porosity of the lignocellulosic sample as observed in the determined porosity of the material showed in Table 1.

It was observed that when the acetylated OPEFB was used for crude oil sorption, crude oil was mainly sorbed at the medium and large size pores. This is because Fig 4c showed that the average size of the small pores (0.41 μm^2) was unaffected after crude oil sorption while that of the medium and large pores reduced significantly from 7.75 and 812 μm^2 (Fig. 4b) to 5.76 and 293.07 μm^2 (Fig. 4c), respectively. Onwuka *et al.* (2016) reported similar findings for acetylated POBPs.



(a) (b) (c)

Fig. 4: Pore histogram for unmodified (a), Modified (b) and modified crude oil treated (c) OPEFB



(a) (b) (c)

Fig. 5: Pore histogram for unmodified (a), Modified (b) and modified crude oil treated (c) CP

Figure 5a – c showed that unlike in OPEFB acetylation, CP acetylation increased the average sizes of the small, medium and large pores in the sample from 0.41, 15.53 and 977.85 µm^2 to 1.71, 23.19 and 1270.27 µm^2 respectively. This implies that acetylation increased the surface area of CP better than that of OPEFB and POBP. However, it was observed in Table 1 that the porosity of CP reduced after acetylation and this could suggest the presence of high number of small size pores after acetylation of CP. Thus, acetylation effect on the porosity of lignocellulosic samples depends on its (acetylation) effect on the pore matrices of the samples. When the acetylated CP was used in crude oil sorption, it was observed that it was the average small pore sizes that highly sorbed the crude oil. This is because the average size of the small pores reduced significantly from 1.71 to 0.31 µm^2 while that of the medium and large pores further increased. The increase in the average size of the medium and large pores could be attributed to the partly sorption of crude oil on the surface of these pores and thus, leaving broad pores for measurement by the machine.

This result showed that acetylation increases the surface area of the lignocellulosic samples by opening up some of the pores and the extent of increase or decrease in the size of the different pores by acetylation, depends on the nature and compositions (surface wax, hemicellulose and lignin) of the lignocellulosic sample.

Conclusion

This study showed that acetylation does not significantly affect the inorganic composition of lignocellulosic samples. However, acetylation significantly affects moisture content, porosity, densities (bulk and particle densities), crystallinity index and pore sizes of lignocellulosic material. Acetylation reduced the moisture content, bulk densities (compacted and uncompacted) and crystallinity index of the lignocellulosic samples (OPEFB, POBP and CP). The particle density and porosity of POBP were increased by acetylation while those of OPEFB and CP were reduced.

Pore analysis showed that the lignocellulosic samples are made up of mostly small pores with few medium and large pore sizes and acetylation affects the pore matrices of lignocellulosics. The extent to which the sizes of the small pores are reduced or increased by acetylation, affects the overall porosity of the lignocellulosic samples despite the fact the acetylation mainly increase the average size of medium and large pores. Thus, acetylation improves the composite and oil spill cleanup application properties of lignocellulosics as reinforcements in plastics and oil sorbents in aqueous medium, respectively.

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All authors have endorsed the publication of this research.

Availability of Data and Materials

All data and materials relevant to this article has been included

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The authors declare that they have no competing interests.

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Author's Contribution

Jude Chinedu Onwuka designed the research; *Jude Chinedu Onwuka and Emeka Elias Elemike* carried out the XRD and pore size analysis while *Jude Chinedu Onwuka, Nasirudeen, Mohammad Baba, Hashim Ibrahim and Yusuf Biki Nale* carried out the physicochemical analysis. All *Authors* interpreted the results and participated in the writing of this research article.

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