Acetylation of Wood Flour from Four Wood Species Grown in Nigeria Using Vinegar and Acetic Anhydride

Yakubu. Azeh[1]

Gabriel. Ademola. Olatunji[2]

Cheku Mohammed[3]

[1]Chemistry Department, Ibrahim Badamasi Babangida University, Lapai. Nigeria
[2]Chemistry Department, University of Ilorin, Ilorin. Nigeria
[3]Chemistry Department, Ibrahim Badamasi Babangida University, Lapai. Nigeria

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Abstract

Effect of acetylation on pre-treated wood flour of different wood species, Boabab (Adansonia Digitata), Mahoganny (Daniella Oliveri), African locust bean (Parkia Biglobosa) and Beech wood (Gmelina Arborea), has been investigated. Acetylation was carried out in batches using acetic anhydride and then with commercial vinegar in the presence of varying amount of $CaCl_2$ *as catalyst and at temperature of 120 °C for 3 h under reflux. The success of acetylation was determined based on Weight Percent Gains. FT-IR spectroscopy, a veritable tool was used for the analysis of both treated and untreated samples to further investigate the success of acetylation. The results showed the presence of important band such as carbonyl absorptions at 1743, 1744, 1746, 1731, 1718 and 1696* cm^{-1} *as appeared separately in the spectra of acetylated samples, confirming esterification occurred. The purpose of this work was to investigate the applicability of vinegar for acetylation of lignocellulosic fibers. Acetic anhydride is a common acetylation reagent, but its utilization is restrictly prohibited in some countries. Using commercial vinegar as an alternative reagent was quite novel and interesting. Blends/composites were prepared by solution casting and their kinetics investigated in distilled water. The results indicated they could be used in outdoor/packaging applications.*

Keywords: *Acetylation, vinegar, acetic anhydride, wood flour, composites/blends.*

1. introduction

Composites have been described as materials composed of a hard material with discontinuous reinforcement that is embedded in a weaker, continuous matrix. The reinforcement matrix (Supri and Lim, 2009) maintains the position and orientation of the reinforcement. The constituents of the composites retain their individual, physical and chemical properties. Composites give a combination of qualities that are very different from the individual constituents that constituted the composite. Several reports on thermoplastic composites have been documented. Different types of modified and unmodified natural fibres such as wood fibers and flour, kenaf fibers, sago, rice starch, cornstarch, henequen fibers, and pineapple-leaf fibers, have been used as fillers in polymer matrices (Supri and Lim, 2009; Azeh *et al*, 2012).

Dimensional stability and strength of unmodified wood flour polyethylene composites was reported to have improved by increased in fibre loading(s). Unmodified starch has been used to produce composites of low density polyethylene (LDPE). Composites of unmodified starch have been reported to exhibit low mechanical properties, though with improved biodegradation. The introduction of ester groups unto starch surface, manipulate its properties and support the blending mechanism (Sriroth, 2000). Wood-Plastic composites have been described as products form by combining treated or untreated wood in the form of fibre or particles and a thermoplastic polymer such as polyethylene, polyvinyl Chloride or polypropylene (Kristoffer *et al*, 2012). Wood-plastics have significant applications in various fields such as construction / engineering. Wood as a construction material, its use is impaired under certain degradative agents due to its hydrophilic nature, presence of cellulose, a food substrate for micro-organisms. For this reason, interest in eco-friendly methods to improve the performance of wood are been developed. All over the world, efforts are been made to move away from toxic to non-toxic means of wood modification.

Chemical modification of wood is a very good alternative to conventional wood preservation methods. Acetylation has received considerable attention more than any other chemical modification techniques known (Rowell *et al*, 1994). This method not only protect wood/wood based products against degradative agents, but also changes the hydrophilic nature of the wood components (Cellulose, Hemicelluloses and Lignin) to hydrophobic by increasing the acetyl contents in the polymers while decreasing their ─OH groups. This, therefore, enhances the surface energy and interfacial interaction between acetylated wood-dust and the hydrophobic polymers. It has been reported that for every acetyl gain, one ─OH group is eliminated. Implying, there is a reduction in hydrogen bonding within the wood reactive polymers. This can increase the interfacial bonding of PE with the acetylated wood surface (Frihart *et al*, 2004). Since, the surface qualities play a significant role to satisfactory interfacial performance; we therefore, acetylate four different wood flour of four wood species grown in Nigeria using acetic anhydride and as well investigate the feasibility to use commercially available vinegar for acetylation of cellulose in lignocellulosic materials because of its low cost, availability and renewability. Acetylation of cellulose in wood flour was carried out in the presence of varying amount of $CaCl_2$ as catalyst to manipulate its properties in order to support the blending mechanism. The objectives of this work were to investigate the feasibility of vinegar for acetylation, preparation of blends/composite and investigation of their sorption kinetics in distilled water for application in industry.

2. Materials and Methods

Wood flour used were from four wood species Baobab (*Adansonia Digitata*), Mahoganny (*Daniella Oliveri*), African locust bean (*Parkia Biglobosa*) and Beech wood (*Gmelina Arborea*) collected from a saw-mill located in Niger State - Nigeria. Reagents and chemicals used were obtained from May and Baker and these include; Commercial Vinegar, Acetic anhydride, NaOH, ethanol, toluene, sulphuric acid, hypochlorite, $CaCl_2$. All reagents used were of analytical grade.

3. Soxhlet Extraction

To reduce the influence of wood extractives on the acetylation, 5 g of 2 mm size wood particles were extracted with a mixture of ethanol-toluene (2 : 1 v/v) for 3 h. After extraction, samples were rinse with ethanol followed by hot water and then oven-dried at 105 ^{O}C for 24 h to reach constant weight. Extractible content was calculated as a percentage of oven-dried test samples.

4. Sample Pre-Treatment by Mercerization

Mercerization of 2 g oven-dried extracted sample was mercerized using 20 mL of 10 % NaOH solution. The mixture was placed on a shaker and shake at 75 rpm for 1 h. The sample was washed with distilled water until it was neutral. The residue was oven-dried at 105 ^{O}C for 1 h. The procedure was repeated for each wood flour sample.

5. Chemical Modification

5.1 Acetylation

Acetylation was carried out in batches. The first batch was conducted using acetic anhydride while the second batch was carried out using commercial vinegar as acetylating agents in the presence of varying amount of $CaCl_2$ as catalyst. 2 g of oven-dried samples of wood species oven-dried at 105 ^{O}C with a constant weight (wunt) were treated with the acetylating chemicals each with 0.5, 1 g $CaCl_2$ catalyst at 120 ^{O}C during 3 h refluxing. After modification, the residues were thoroughly washed with distilled water until neutral and then oven-dried for 3 h. The extent of acetylation was calculated as weight percent gains (WPGs) based on the differences in oven-dried weight of the samples before and after modification (Wunt) and after modification (Wtrt) according to the equation;

6. Blending Procedures

The dissolution of high density polyethylene (packaged water sachets) follows the method described by (Abdulkareem *et al*, **2005**). In brief, 1 g pieces of non-printed portion were placed in a reaction flask and 30 mL of toluene was added. The content was placed on a hot plate at 100 ^{O}C, and a thermometer was inserted. The sachets swelled at 60 ^{O}C, and then rapidly dissolved at 80 ^{O}C to give a clear solution. Blending of high density polyethylene and acetylated wood flour is thus described. Into the clear solution of high density polyethylene sachets was introduced 0.5 /1.0 g of each vinegar / acetic anhydride treated or untreated wood flour while stirring for 5 min and then spread on clean metal plates to form a film. The thin films formed were peeled-off the metal plates to afford acetylated wood flour / polyethylene blends (Azeh *et al*, **2012**).

7. Water Absorption Test of Acetylated and Untreated Blends

Three sets of specimens were prepared. Acetylated blends and untreated blends were subjected to water absorption test. The blends were soaked for 1, 2 and 16 h respectively. After each immersion, the blends were removed and wipe off using filter paper and then weighed and weight were noted.

Using the formula $\frac{H2-H1}{H1}\, X\, 100\,\%$

Where H1= Initial weight of blend before immersion in water and H2 = Weight of blend after immersion in water.

8. Fourier Transform Infrared Spectroscopy Analysis

The properties of acetylated and untreated samples were characterized using FT-IR, Perkin-ELMER-8400S Spectrophotometer in the range 4000 cm-1 to 400 cm-1. Samples were run using the KBr pellet technique at the National Research Institute for Chemical Technology (NARICT), Zaria, Kaduna-Nigeria.

9. Results and Discussion

Table 1. Assignment of the IR spectra bands of functional groups in acetylated wood flour treated with acetic anhydride.

Band position (cm -1)	Functional group
3973–3352	-OH bonded stretching vibrations

1746–1731	C=O stretching vibrations of acetate group
2938–2917	C–H methyl and methylene groups.
1373–1369	(- C-CH3 -) in acetate group due to acetylation.
1285–1241	(v**C-O**) stretching band vibrations of the acetyl moieties
1628–1618	─OH of absorbed water.
1527- 1511	(C=C), Aromatic skeletal absorption caused by lignin.
1044–1042	C–O stretching vibrations in cellulose, hemicelluloses and primary alcohol.
1052	C – O stretching in acetyl (Covalence vibration).
620–603	C–H out of plane stretching absorption of aromatic ring vibrations caused by lignin.

Table 2. Assignment of the IR spectra bands of functional groups in acetylated wood flour treated with Vinegar based on acetic anhydride and ketene related work.

Band position (cm -1)	Functional group
3978–3111	–OH stretching (bonded) vibrations
1718	C=O stretching vibrations of acetate group
1696	C=O stretching in acetyl groups
2723 and 2820	C–H stretch of methylene in celluloses and hemicelluloses
2928–2904	CH$_3$ symmetric stretch of methyl groups of aliphatic.
1350–1340	(-C-CH$_3$-) deformation of acetate group in cellulose and hemicelluloses
1254–1247	(vC-O) stretching band vibrations of the acetyl moieties and (C=O)
1629–1624	deformation in the ester bond during acetylation.
1654	C=C stretching of aromatic ring of syringyl in lignin.
1527–1509	C=O stretching of (COOH) in glucoronic acid.
1044–1042	C=C Stretching of the aromatic ring caused by lignin.
1439–1428	C–O stretching vibrations in cellulose, hemicelluloses and primary alcohol
625–603	CH$_2$ deformation and stretching in Cellulose, Lignin and Xylan.
	C–H out of plane stretching absorption of aromatic ring vibrations caused by lignin.

The IR spectra of acetic anhydride or vinegar treated wood flour showing the major absorption bands are shown in table 1 and 2 above. The following strong absorption bands as reflected separately on the IR spectra of vinegar treated wood flour are characteristic absorptions of bonded –OH and these include, 3978-3339, 3477-3375, 3426-3360, 3907-3372, 3429-3387, and 3874-3111 cm^{-1} (Azeh *et al*, 2012; Tuong and Li, 2010; Mohebby, 2008). The following peak intensities at 3029, 3104, 3345, 3602, 3352, 3852 and 3938 cm^{-1} as reflected separately on the IR spectra of acetic anhydride treated wood flour are characteristic absorptions of bonded ─OH group stretching vibrations in cellulose and hemicelluloses. Acetic anhydride or vinegar treated wood flour showed reductions in ─OH absorption bands. The ─OH absorption bands of untreated wood flour were predominantly detected at 4008, 4055, 4107, 4290, 4394, 4413, 4567, 4570, 4685 and 4696 cm^{-1} . The intensity of the ─OH absorption bands in treated samples decreased. This decrease in intensity of ─OH band is an indication that, the hydroxyl group contents in wood flour were reduced during reaction. Indicating that some level of acetylation had taken place (Azeh *et al*, 2012; Bodirlau and Teaca, 2007; Mohebby, 2008). The presence of ─OH absorption in vinegar/acetic anhydride treated wood flour has been attributed to hydroxyl functionalities that are not accessible to chemical reagent (Callum, 2002). The band at 1746–1731 cm^{-1} as reflected on acetic anhydride treated wood flour is a characteristic absorption of carbonyl (C=O ester) stretching vibration of acetate group in cellulose and Uronic ester in hemicelluloses. This band showed evidence of acetylation (Bodirlau and Teaca, 2007; Nasar *et al*, 2010; Mohebby, 2008; Adebajo and Frost, 2004; Indrayan *et al*, 2000; Morrison and Boyd). The peak absorption increased in acetic anhydride treated samples, indicating high level of acetyl gain as shown in Table 3. While vinegar treated samples showed this band at 1718 cm^{-1} and 1696 cm^{-1}. The low level of acetylation could be attributed to low percent acetyl content in vinegar and shorter reaction time adopted for acetylation. Since, vinegar treated Baobab sample gave 11.61 % (WPG) during four hour reaction unlike other samples who gave less than 11.61 % during 3 h reaction as reflected in Table 3. This implies that, longer reaction times are required for acetylation using vinegar. 1696 cm^{-1} carbonyl (C=O) absorption peak have been reported in ketene treated wood cellulose (Azeh *et al*, 2012). The peak here has been attributed to low penetration of acetyl. Consequently leading to lower percent gains. The absorption band at 2723 cm^{-1} and 2820 cm^{-1} observed in vinegar treated samples have been assigned to C-H stretching vibrations of $—CH_2$ and $—CH_3$ groups in cellulose and hemicelluloses (Azeh *et al*, 2012; Adebajo and Frost, 2004). The presence of absorption peaks at 2938- 2091cm^{-1} reflected on acetic anhydride and 2928-2904 cm^{-1} in vinegar treated samples have both been assigned to asymmetric stretching vibration of aliphatic $—CH_3$ group which is evidence of acetylation (Azeh et al, 2012; Tuong and Li, 2010; Nasar *et al*, 2010; Nada *et al*, 2009; Cetin and Ozmen 2011). The small bands at 1628–1618 and 1629–1624 cm^{-1} in acetic anhydride or vinegar treated samples are assigned to adsorbed water, β-glucosidic linkages (ether - C–O–C -) in the cellulose chain or sugar units or could be due to aromatic ring (C = C) vibrations in lignin (Syringyl) (Azeh *et al*, 2012; Bodirlau and Teaca, 2007; Nasar *et al*, 2010; Mohebby, 2008; Callum , 2002). The absorption bands at 1527 –1509 cm^{-1} are characteristic absorption of aromatic (C=C) stretching vibrations caused by lignin (Guaiacyl) (Azeh *et al*, 2012; Bodirlau and Teaca, 2007; Tuong and Li, 2010; Nasar et al, 2010; Mohebby, 2008; Callum, 2002). This suggests the presence of lignin (Mohebby, 2008; Callum, 2002). The bands at 1439–1428 cm^{-1} are due to C-H deformations and bending vibrations of $—CH_2$ (methylene) in cellulose and hemicelluloses (Azeh *et al*, 2012; Morrison and Boy`d; Sandak *et al*, 2009; Adebajo and Frost, 2004; Sikorki *et al*, 2004). These bands were not found in acetic anhydride treated wood flour. The reason could be that, longer reaction time adopted led to product (cellulose/hemicelluloses) degradation and subsequently their extraction by acetylating chemical occurred and was probably washed alongside with the by-products. An important band which showed that some level of acetylation was achieved by the two reagents used for acetylation were observed at 1330-1373 cm^{-1} for acetic anhydride and 1340-1348 for vinegar. This important band was attributed to aliphatic C-H deformation/bending vibration of $—CH_3$ in acetyl and this is evidence of the formation of ester bond due to acetylation in cellulose and hemicelluloses (Azeh *et al*, 2012; Bodirlau and Teaca, 2007; Mohebby, 2008; Indrayan *et al*, 2000). This absorption peak was missing in control samples. A prominent absorption band which further gave evidence of acetylation appeared at 1285-1242 cm^{-1} for acetic anhydride while 1254-1247 cm^{-1} peak absorption was detected for vinegar as alternative and novel acetylation agent. This band has been assigned for stretching of C—O and deformation of C=O in the acetate bond formed during acetylation in xylan and lignin (Tuong and Li, 2010; Indrayan *et al*, 2000; Mohebby, 2008; Adebajo and Frost, 2004). The absence of absorption band at 1800–1760 cm^{-1} in all the spectra of acetic anhydride treated samples was an indication that, the acetylated products were free of unreacted acetic anhydride, implying that the reagent was used-up during the reaction. While the absence of absorption peak at 1700 cm^{-1} in all spectra is evidence of the absence of unreacted carboxylic acid in vinegar treated samples and as a by-products in acetic anhydride treated wood flour respectively. The bands at 1044–1042 cm^{-1} are assigned to C–O stretching vibrations in cellulose, hemicelluloses and that of primary alcohol (Azeh *et al*, 2012; Bodirlau and Teaca, 2007; Nasar *et al*, 2010; Mohebby, 2008). The medium band at 1052 cm^{-1} ascribed to C-O stretching vibration of acetyl group in acetate (Azeh *et al*, 2012; Morrison and Boy`d; Nasar *et al*, 2010) is evidence of acetylation.

Table 3: Average Weight Percent Gain (WPG) in Vinegar and Acetic Anhydride Treated Wood Flour

Sample	Acetic anhydride (%)	Sample	Vinegar (%)
Gmelina	17	Gmelina	10.8
Mahogany	12	Mahogany	8.5
Baobab	19	Baobab	11.61
Locust bean	7	Locust bean	10.5

9.1 Water Absorption Kinetics of Acetylated and Control Wood Flour Samples.

Table 4: Percent of water absorption after soaking for 1, 2 and 16 hours.

S/N	Blend Sample	Dry weight (g)	Weight after soaking/h 1h, 2h, 16h.	Percentage of water Absorption (%)/h 1h 2h 16h.
1	Acetic anhydride treated blends	1.00	1.08 1.16 1.38	8 16 38
2	Acetic anhydride untreated blends	1.00	1.34 1.39 1.49	34 39 49
3	Vinegar Untreated blends	1.00	2.70	70
	Vinegar treated blends	1.00	1.52	52

Three sets of specimens were prepared, as shown in table 3 above. Blends prepared from acetylated wood flour were flexible, brittle and very smooth and absorbed less water compared with untreated blends which were coarse with rough surface. Modification of fibre surface really help to manipulate its properties and supports the blending mechanism as was observed on blends made from treated wood flour. It has been established that when the accessible hydroxyl groups in the cell wall polymers have been substituted by acetyl, reduction in water and moisture sorption are observed, and this depends on the level of acetylation too. The results also showed that, water absorption of blends is dependent on fibres in the matrix. It is expected that, the sorption rate for 16 h soaking duration should give about 16 times the results obtained for 1 / 2 h soaking periods. However, this was not observed. Indicating that, the fibres in the polymer matrix have reached their saturation point and thereby cannot absorb much water molecules. Acetylated blends reached fibre saturation point faster compared to untreated blends as indicated by the percent water uptake / sorption rate in tables 3. This is attributed to modification of the hydrophilic fibre surface by acetyl moieties and subsequent hydrophobicity improvement of fibre surface which allowed for proper interfacial bonding with polyethylene.

9.2 Results of the Formation of Blends

Blends obtained from the incorporation of acetylated wood flour with polyethylene were flexible and had smooth surface (Figures 1a and 1b). These blends were easily peeled-off the film forming plate while those obtained from untreated wood flour were porous, coarse and were difficult to peel-off from the film forming plate. For this reason, blends had rough surface (Figure 1c). Poor blend formation exhibited by untreated wood flour could be attributed to facial differences between the two materials- hydrophilic biopolymers in wood flour and the hydrophobic polyethylene, causing very poor interfacial interaction between the materials (Azeh *et al*, 2012). Treated wood flour resulted in the formation of flexible blends with smooth surface after incorporation and solution casting on metal plates. The properties exhibited by these blends was an indication that, acetylation using vinegar and acetic anhydride successfully transformed accessible hydrophilic hydroxyl surfaces of the biopolymers in wood flour to hydrophobic surface (acetyls) which causes proper interfacial interaction with polyethylene as reported by (Azeh *et al*, 2012; George *et al*, 1998; Azeh *et al*, 2012).

Figure 1a. Photographic Plate of Acetylated Blend (1 g Wood flour / 1 g Polyethylene Loading)

Figure 1c. Photographic Plate of Acetylated Blends (0.5 g Wood flour / 1 g Polyethylene Loading)

Figure 1b. Photographic Plate of Untreated Blend (0.5g Wood flour / 1 g Polyethylene Loading)

10. Conclusion

In this work we have been able to carry out acetylation of cellulose in wood flour using vinegar successfully. Results of the kinetic studies of blends indicated that, treated blends had lower water sorption than untreated blends. Because treated blends had lower hygroscopic surface with a high hydrophobic energy surface that facilitated its interaction with polyethylene during the blending process. While untreated blends had high water sorption, due to the presence of accessible hydroxyl groups in cellulose and other biopolymers in wood which allowed for strong formation of hydrogen bonds with water molecules. Treated wood flour blends could be very useful in outdoor applications such as decking and packaging. Further work on the use of vinegar as acetylating agent is recommended based on the results reported in this work.

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