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Ketene Acetylated Wood Cellulose for Industrial Applications in Wood-base and Polymer Industry

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ABSTRACT

Cellulose-polyethylene blends were produced and the effects of acetylated cellulose on the biodegradability of blends were investigated. Ketene obtained by pyrolysis of acetone over various heated metals which include Zn, Mg, Cu, Fe and ZnS (sphalerite) from a specially modified apparatus used to acetylated wood and industrial cellulose increased surface interaction between the hydrophobic acetylated cellulose with non-polar hydrophobic polyethylene. The results indicated that the acetylation successfully eliminated most accessible hydroxyl groups in the samples as indicated by IR and NMR Spectra data. The blends produced from acetylated cellulose showed improved dimensional stability and reactivity attributed to surface interaction between acetylated cellulose (hydrophobic) and hydrophobic polyethylene. The biodegradation test indicated that the incorporation of acetylated cellulose into polyethylene enhanced their biodegradability implying that acetylated cellulose in poly-products will be a good control measure for pollutants from poly-products. The properties of modified wood cellulose were enhanced, due to lower equilibrium moisture content caused by acetyl groups. Modified wood cellulose could find industrial applications in fiber and particle/plywood board products for various construction purposes while modified cellulose-based materials can be used in the production of polymer-based biodegradable products.

Key words: Acetylation, cellulose, wood cellulose, pyrolysis, ketene, cellulose-polyethylene blends

INTRODUCTION

Wood is considered as a very friendly and useful raw material used extensively for various construction purposes. Wood is a bio-polymer with a complex structure and constituting cellulose, lignin and hemicelluloses. These bio-polymers make up the cell wall and determine the basic chemistry in wood which explains most of the physical and chemical changes that are observed in wood and wood-based products. But certain degradative environmental factors restrict wider applications of this bio-polymer. To improve the performance of this bio-polymer for wider applications, the basic functionalities (-OH groups in the cell-wall) must be transformed in order to have wood with improved properties for durability and stability (Rowell, 2006; Han *et al.*, 2009). In order to achieve this, various modification methods have been developed. These include chemical and heat treatment methods. Of these methods acetylation of wood and lignocellulosic fiber has been widely studied simply because it's a single site reaction that transforms the properties of the natural bio-polymers to afford wood products with a variety of promising properties for various applications for sustainable development (Hill, 2002). Ketene was first used in 1945 to acetylate wood, with small Weight Percent Gain (WPGs) in acetyls . Another study was also reported on the use of ketene to acetylate different species of wood, where up to 25% Weight Percent Gain (WPGs) in acetyl were obtained (Rowell *et al.*, 1986). There have been many reports on acetylation of wood and lignocellulosic fibers using different acetylating agents and catalysts at various reaction times. On these reports, various spectroscopic techniques such as IR, Solid state NMR (^{1}H and ^{13}C), ATR-IR, CP-MAS-C-13NMR have been used for structural elucidation of wood and acetylated products (Ahmad *et al.*, 2005; Bodirlau *et al.*, 2007; Adebajo and Frost, 2004; Homan and Jorissen, 2004; Badal *et al.*, 2005; Sikorski *et al.*, 2004; Sassi *et al.*, 2000; Vick and Rowell, 1990). Wood is gaining more industrial attention and it is used as mulch, fabrication of particle board for modern furniture, domestic uses to support combustion of fire woods in cooking, compost of wood dust is also use as manure by many peasant farmers etc. Wood dust has limited industrial applications. In order to find possible industrial applications of this bio-polymeric material, wood cellulose extracted from various wood dust was acetylated. Industrial cellulose was also acetylated for comparative studies. In our efforts to generate ketene and use it for acetylation, a modified apparatus was adapted for the pyrolysis of acetone over heated metals including (Zn, Mg, Cu, Fe) and ZnS mineral. The ketene generated was used to modify wood cellulose and industrial cellulose by acetylation.

MATERIALS AND METHODS

Thin layer Chromatography, (TLC) plates were studied under the short wavelength of the UV-lamp (256 nm) and 366 nm (long wave length). Infrared spectroscopy and nuclear magnetic resonance spectra were recorded on a Perkin-ELMER instruments 100 X FT-IR run as KBr Pellets disk over the spectral range 4000 cm to 500 cm^{-1}. Proton and C-13NMR Spectra were recorded on a BRUKER AC 200 MHz spectrometer using $CDCl_3$ (for CCF/8, 9, 10) and d6-DMSO (for KET-CELL. and WDRF) as solvent. The cellulose and wood cellulose used were obtained as gift from another research group and used without further purification. Acetone, dichloromethane, n-hexane, petroleum ether, diethylether, methanol used were of analytical grade. Metals used include Fe, Zn, Cu, Mg and ZnS mineral (sphalerite). Anhydrous magnesium sulphate was used to dry solutions. Acetone was distilled twice for optimal purity.

Mercerization of wood cellulose: One gram of wood cellulose was mercerized with 5% of 20 mL NaOH solution. The suspension was mechanically stirred for 15 h for ketene up-take and subsequent functionalization of the biopolymers.

Apparatus description: The apparatus adapted for the generation of ketene is a modification of the conventional apparatus (Williams and Hurd, 1939; Harriott, 1933) where a thermal chamber replaced the electrical chamber. The novelty in this work is that, the use of metals and thermal chamber provides a short contact time for ketene generation and subsequent high yield attributed to close packing of metals in 5 mm internal diameter and 3 cm long packing in a pyrex glass combustion tube than conventional apparatus whose filament is 70 cm long, sealed in a pyrex glass, 25 cm long with 70 mm internal diameter.

Table 1: Ketene-M. wood-cell and ketene-cell acetylation products

KMW-CELL	KET-CELL
KMWCF Mg	KCF Mg
KMWCR Mg	KCR Mg
KMWCF Zn	KCF Mg
KMWCR Zn	KCR Mg
KMWCF Cu	KCF Zn
KMWCR Cu	KCR Zn
KMWCF ZnS	KCF Cu
KMWCR ZnS	KCR Cu
KMWCF Fe	KCF Fe
KMWCR Fe	KCR Fe

KMWCF: Ketene-mercerized wood cellulose filtrates, KMWCR: Ketene-mercerized wood cellulose residue, KCF: Ketene-cellulose filtrates, KCR: Ketene cellulose residue

Acetylation: One gram of wood cellulose was pre-treated with 20 mL of 5% NaOH, stirred for 15 h on a magnetic stirrer. A viscous suspension was obtained which was transferred into the reaction flask. The iron pipe adapted as the furnace was pre-heated for 5 min (to increase heating efficiency of the apparatus), after which 40 mL of dry acetone was distilled. This process generated the ketene that was used to acetylate the samples. The mixture was cool to room temperature while stirring with a magnetic stirrer. It was filtered and the residues washed until neutral with distilled water and then air dried. The filtrates had two layers and were separated using a separating funnel and stored at room temperature for further treatment. The dried residues were milled in a porcelain mortar and sieved through a 2 mm size nylon sieve. The fine particles were collected and stored at room temperature prior to IR and NMR analyses. Other wood cellulose acetylation products were obtained from metals (magnesium turnings, zinc filings, copper filings and sphalerite dust) using the process previously described. All the products obtained were assigned codes as shown in Table 1.

TLC test: The mixture of the acetylation products were spotted on a TLC pre-coated plates and developed in n-hexane-diethylether (1:1). After each plate had been developed, the plates were viewed under the UV-lamp at 256 nm. The spots were noted. Colour visualization test was carried out on the TLC plates with vanillin spray reagent and then heated. Blue and orange colour were observed separately on KCF Mg and KETENE-M.WOOD-CELL, respectively.

The organic layer of the acetylation products was chromatographed on a silica gel packed column using n-hexane-diethylether (1:1) as eluent to obtain twenty five (25) fractions of 100 mL each. The fractions were checked by TLC, with n-hexane-diethylether (1:1) as developing solvent and thereafter, sprayed and heated. The spots were noted and the R_f values calculated. Identical fractions were combined and concentrated to recover the solvent and then preserved prior to use. A TLC analysis showed column chromatographic fractions 8, 9 and 10 to be pure components. Each of them showed as a single spot with R_f of 0.54 in n-hexane-diethyl ether (1:1) on the chromatogram.

Ketene cellulose (Mg-generated) was also chromatographed using n-hexane/diethylether (2:1) as eluent to obtain 8 fractions of 50 mL each coded CC1-CC8. These fractions were checked by TLC using n-hexane-diethylether (2:1) for development. The plate was sprayed and heated. TLC result showed this to be a mixture. It was therefore, discarded.

Solvent extraction of unmodified wood cellulose: Two gram of wood was mercerized using 5% of NaOH and stirred on a magnetic stirrer for 15 h. The mixture was filtered, neutralized with HCl and extracted with 2×25 mL of DCM in a separating funnel. The extract obtained was dried with anhydrous $MgSO_4$. The concentrated extract was spotted along side XIV, XV and XII (column chromatographic fractions 9, 10 and KMWCFM g) on a pre-coated TLC plate, developed in 1:1 n-hexane-diethylether mixture and examined under the UV-lamp at 256 nm. The spots were noted. The plate was thereafter, sprayed with vanillin spray reagent and heated. The colour was noted. Solvent extraction of the aqueous portion of Fe and ZnS acetylation products of wood cellulose. The reaction mixture formed two layers (organic and aqueous). The aqueous layers of each product obtained was separated from the organic and neutralized with HCl and extracted with 2×25 mL of DCM. The extract was dried with anhydrous $MgSO_4$, concentrated and stored for further treatment. Concentrated extract was spotted along side XIII, XV (unmodified wood cellulose mercerized and CC/10) on a TLC plate, using n-hexane-diethylether (1:1) as developing solvent. The plate was examined under the UV-lamp at 256 nm. The spots were noted. The plate was sprayed with vanillin and heated. The colour reaction was also noted.

Water absorption test of acetylated samples and controls

Preparation of plywood tablets: Plywood tablets (2×2 cm) were prepared and the weight of each tablet was noted. Acetylated and control wood cellulose residues (150 mg) were mixed with 0.7 g adhesive. The mixture was spread uniformly in-between two plywood tablets, pressed together for 15 min at room temperature and excess adhesive wiped out. The tablet was weighed and allowed to air dry for 16 h. over night and then re-weighed. The plywood tablets were soaked in water for 3 h excess water was wiped off and the new weight were taken. The percentage weight increase due to water absorption was calculated based on the original weight of the air dried plywood tablets.

Dissolution of polyethylene (packaged water sachet) and incorporation of acetylated cellulose and wood cellulose: Polyethylene (Packaged water sachets) was collected from the University of Ilorin, Ilorin, Nigeria main campus. Dissolution of the polyethylene sachets follows the method previously adopted (Abdulkareem and Garba, 2005). Into this, solution was introduced 0.5 g of each ketene treated and untreated cellulose and wood cellulose separately 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 cellulose and wood cellulose-polyethlene blends.

Biodegradability test of blends: Untreated cellulose, acetylated wood cellulose and treated cellulose polyethlene blends were subjected to biodegradation, fungal and bacterial test. This was carried out by taking a 5×5 cm sheet and burying them under the ground with moist condition. The sheets were taking out after 2 weeks and thereafter, 16 weeks and assessed for biodegradation using appearance, brittleness, perforation and weight loss parameters.

RESULTS AND DISCUSSION

The FT-IR spectra data of non-acetylated (wood cellulose and cellulose) and acetylated (m-wood cellulose and cellulose) samples indicating the major absorption bands are shown in Table 2. The strong absorption bands at 3843.09, 3739.66, 3734.33, 3733.83, 3731.23, 3614.99, 3427.51 and 3316.16 cm^{-1} as reflected separately in all the IR spectra are characteristic absorptions of

Table 2: IR Spectra band assignments of acetylation products based on related literature (Hill, 2002; Rowell, 2006; Mohebby, 2008; Nada *et al.*, 2009)

Frequency (cm^{-1})	Assignments
3316.16-3843.09	-OH bonded stretching vibrations
2923.04-2924.74	CH_3 asymmetric stretching of aliphatic
2873.28	C-H stretching vibrations in cellulose and hemicelluloses
1691.31-1692.30	C=O stretching of acetate group
1633.25	C=C benzene ring vibrations in lignin
1518.52-1518.66	C=C absorption of aromatic skeletal vibrations caused by lignin
1419.78-1452.38	C-H deformations and bending vibrations of CH_2 in cellulose and hemicelluloses
1373.78	C-H deformations of CH3 group in Acetyl
1072	C-O stretching of acetyl group in acetate
1014.4	C-O stretching vibrations in cellulose, hemicelluloses and primary alcohol

bonded-OH groups. The acetylated wood cellulose showed a reduction in -OH absorption band at 3733.83 and 3316.42 cm^{-1}. This is an indication that, significant level of acetylation occurred (Rowell, 2006; Mohebby, 2008). Wood cellulose is a polymer with high hydroxyl functionality and for this reason, chemical modification is not always sufficient enough to eliminate all the -OH functional groups (Hill, 2002). The band at 1027.25, 1014.40 and 1024.96 cm^{-1} are ascribed to C-O stretching vibrations in cellulose, hemicelluloses and that of primary alcohol (Sandak *et al.*, 2009; Mohebby, 2008). Another important band that showed evidence of acetylation is the C=O stretching of acetate group at 1691.31 and 1692.30 cm^{-1} in the spectra of acetylated samples. The band at 1072 cm^{-1} is ascribed to C-O stretching of acetyl group in acetate and is evidence of acetylation. The absorption band at 2873.28 cm^{-1} has been assigned to C-H stretching vibrations in cellulose and hemicelluloses. This band increased in the following acetylated samples: Fractions 9-10 of acetylated wood cellulose (mercerized) organic layer of Fe-generated ketene and acetylated cellulose, showed this peak at 2924.31, 2924.74 and 2923.04 cm^{-1}, respectively. This is due to asymmetric stretching of aliphatic CH_3 group which again is evidence of acetylation (Nasar *et al.*, 2010). The absorption at 1373.78 cm^{-1} (-C-CH_3) in the IR spectra of acetylated wood cellulose sample CCF 9, is attributed to C-H deformation of CH_3 group in acetyl, this confirmed the formation of ester due to acetylation in cellulose and hemicelluloses (Mohebby, 2008; Sandak *et al.*, 2009). The absorption bands at 1554.20, 1518.52 and 1518.66 cm^{-1} are characteristic absorption of aromatic skeletal vibrations caused by lignin. This suggest the presence of lignin in the wood cellulose used (Hill, 2002; Mohebby, 2008). These bands were not found in the cellulose. C=C (double bond) stretching vibrations at 1633.25 cm^{-1} could be attributed to benzene ring vibrations in lignin, this showed the presence of lignin in wood cellulose. The bands at 1421.76, 1419.78, 1457.01 and 1452.38 cm^{-1} which are due to C-H deformations and bending vibrations of CH_2 in cellulose and hemicelluloses, were not found in non-acetylated and acetylated wood cellulose residue (Sikorski *et al.*, 2004; Nada *et al.*, 2009; Nasar *et al.*, 2010). The reason for this could be that, cellulose and hemicelluloses were degraded and at the same time extracted into the organic layer formed after the reaction, since, these bands showed in the IR spectra of column chromatographic fractions. Chemical modification has been used to isolate various cell wall components of cellulose, lignin and hemicelluloses (Rowell, 2006).

The ^{1}H-NMR spectra data of the ketene-acetylated products (Table 3), shows the chemical shifts of acetylated products based on related literature. The proton NMR data indicated clearly the presence of 6 methyl protons of acetyl groups in the range of 1.3-2.4 ppm and the 7 cellulose proton

Table 3: ^{1}H–NMR chemical shifts of acetylated products

Fraction 8	Fraction 9	Fraction 10	WDRF
δ (ppm)			
1.4	1.3	1.6	2.5
1.61	2.2	2.2	3.9
2.2	2.22	2.22	
2.22	2.3	2.216	
2.24	2.4	2.218	
2.31	3.7	3.516	
		3.602	

Key: WDRF: Wood cellulose residue DMSO extracted filtrate, Data of the acetylated products are based on literature (Badal *et al.*, 2005)

Table 4: ^{13}C-NMR Chemical shifts, δ [ppm] of acetylated products

Fraction 8		Fraction 9		Fraction 10	
δ	Assignment	δ	Assignment	δ	Assignment
29.9	CH3 of acetyl	29.9	CH_3 of acetyl	29.9	CH3 of acetyl
30.19	CH3 of acetyl	76.587	C5	76.597	C5
54.595	C6	77.226	C3	77.226	C3
76.597	C5	77.856	C2	77.864	C2
77.234	C3			97.074	C1
77.871	C2				
128.377	Aromatics				

Acetylated products are as compare with literature references (Heinze *et al.*, 2005; Stewart *et al.*, 2006; Zuckerstatter *et al.*, 2009; Filpponen *et al.*, 2010)

absorbing in the range of 3.52-3.9 ppm. The singlet peak at 7.25 ppm is due to the solvent, deuterated chloroform while the singlet peak at 2.5 ppm for WDRF is due to the solvent, deuterated DMSO (d_6-DMSO).

The C-13 NMR of the acetylated products indicated the presence of an important signal of methyl protons of acetyl groups in the range 29.9-30.19 ppm. The presence of this absorbance is a strong evidence of acetylation. The cellulose back-bone (C_1, C_2, C_3, C_5 and C_6) revealed by C-13 NMR (Table 4) in the range 54.595-97.074 ppm is an indication that the cellulose in the mercerized wood was transformed at morphological level enhancing the uptake of acetylating agent and subsequent functionalization of the accessible hydroxyl groups present in the wood and this, further showed that acetylation occurred. The ^{1}H–NMR analysis of the products indicated a C_4 proton absorbance at 3.60 ppm. The peak maximum at 84 ppm was attributed to C_4 absorbance was found in cellulose. On the contrary, a DEPT spectrum analysis gave an additional proof for cellulose back-bone morphology and acetylation by indicating the presence of 7 protonated carbons (CH-1, CH-2, CH-3, CH-4, CH-5, H_2C-6a and 6b and CH-7 ($CH_3$of acetyl group) which further gave evidence for the structure of the acetylated products. The structure of acetylated product (Fig. 1) was established based on the evidences provided by spectra data as shown in Table 2 and 3 and a DEPT spectrum analysis.

Colour reactions of modified wood cellulose and acetylated cellulose: FT-IR spectra studies of the wood cellulose pointed to the presence of lignin. Therefore, the pink colour reaction could be attributed to interaction between vanillin spray reagent and lignocelluloses present in wood

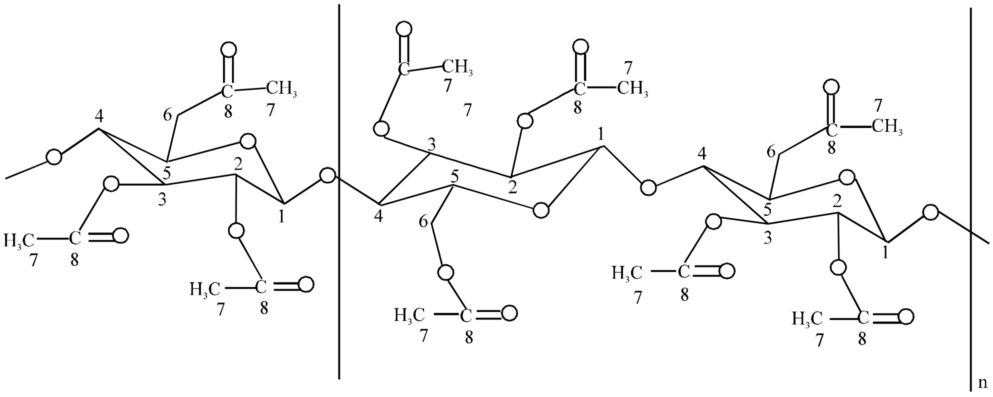

Fig. 1: Structure of acetylated wood cellulose

cellulose. Pink colour reaction has been reported in the study of chloramine reaction with vanillin spray reagent as a means of detecting proteins in cell-wall. Many experiments have been conducted to investigate the compound (s) responsible for the pink colour reaction and it was established that formation of vanillin-chloramine-protein complex came about as a result of reaction of vanillin chloramines which further reacts with proteins within the cell-wall (Wood, 1934). Colour reactions could also be attributed to reactions of acetylated wood cellulose (mercerized) and cellulose with vanillin (phenol), since, coloured compounds are produced when wood/lignin is treated with phenols. Some researchers have suggested the presence of phenolic structures of the type 1,2, 3-trihydroxybenzene nucleus initiated pink colour reactions in woods (Campbell *et al.*, 1937). While the blue colour reaction produced by acetylated wood cellulose (mercerized) could be due to the condensation products of a coniferyl aldehyde group formed with a phenyl propane of lignin in the 6th-position. On the other hand, acetylated cellulose gave orange colour reactions, when sprayed with vanillin spray reagent. The orange colour reactions could be attributed to the presence of indole in cellulose as well as its interactions with acidified solution of vanillin spray reagent resulting in the formation of vanillin derivatives.

Results of the incorporation of dissolved polyethylene (pure water sachet): Acetylated cellulose-polyethylene blends obtained were transparent, brittle and smooth. They were easily peeled-off the film forming plate while those obtained from untreated cellulose were coarse, porous and were difficult to peel-off from the metal plate. The blend formation is due to surface compatibilities between the hydrophobic acetyl groups of acetylated cellulose with polyethylene. Untreated cellulose gave coarse and porous cellulose-polyethylene blends, probably implying the inability of the hydrophilic hydroxyl groups to interact well with hydrophobic polyethylene functionality.

Results of biodegradability test of blends: In our efforts to find industrial applications for acetylated cellulose, cellulose-polyethylene blends were prepared and were subjected to burial test for two weeks and thereafter, 16 weeks. Studies on biodegradability of cellulose blended polyethylene showed that there was microbial adherence to the blends. The biodegradability of blends was studied using physical changes such as appearance, strength, perforation, brittleness and weight loss parameters. After a burial for two weeks, the blends were found to have lost strength but not appreciable and colour changes were observed. Burial for 16 weeks gave appreciable results. The blends degraded appreciably, lost colour and became dark-brown, highly perforated, weight lost increased appreciably from 0.25 to 1.25 g and were no longer transparent and brittle. Bioremediation have been used in the biodegradation of aliphatic hydrocarbon in crude oil (Hidayat and Tachibana, 2012). In the other sector such as petroleum, various authors has evaluated and reported on microbial degradation (bioremediation) of hydrocarbons (Arafa, 2003; Alamri, 2009; Al-Turki, 2009).

CONCLUSION

This research has demonstrated the generation of ketene by pyrolysis of dry acetone over heated metals (Zn, Mg, Cu, Fe and a mineral ZnS (Sphalerite) and described its reactions each with cellulose and mercerized wood cellulose to produce acetylated cellulose and wood cellulose. FTIR, NMR and DEPT spectroscopic techniques were employed to elucidate the acetylation products. The absorption peaks changes in FTIR and the chemical shifts changes in ^{1}H-NMR, ^{13}C-NMR and DEPT of acetylation products, compared to controls is an indication that significant levels of acetylation have been achieved in the experiment. This also confirmed that ketene generation as adapted was successful. Water swelling test on acetylated wood cellulose samples was determined. While control samples indicated 90.55% by weight of water absorption, acetylated samples indicated 65.05%. Therefore, swelling of wood cellulose due to larger space occupied by acetyl groups compared to the space occupied by hydroxyl groups in the cell wall polymers was responsible for the percentage water absorption calculated for each of the sample. In conclusion therefore, the structure elucidated thus far, showed that hydrophilic hydroxyl groups of cellulose as well as mercerized wood cellulose have been substituted with hydrophobic acetyl groups in the cellulose cell wall polymers.

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