

Chemical Modification of Microcrystalline Cellulose: Improvement of Barrier Surface Properties to enhance Surface Interactions with some synthetic polymers for Biodegradable Packaging Material Processing and Applications in Textile, Food and Pharmaceutical Industry

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ABSTRACT

Gaseous acetylation of microcrystalline cellulose (MCC) was carried out to modify its chemical and physical properties and at the same time to preserve the morphology of cellulose microfibrils. Spectroscopic analysis of the samples was indicative of the success of the reaction as indicated by FT-IR and ¹H-nmr studies. The chemically modified microcrystalline cellulose (MCC) were blended with high density polyethylene (HDPE) using novel solvents for dissolution of polyethylene to obtain microcrystalline modified polyethylene blends (MCCMPB). The blends showed improved properties such as, flexibility, smoothness, transparency, strength and biodegradability which is indicative of hydrophobicity improvement relative to non-modified samples. Modification was important so as to bring about changes in attractive and repulsive forces in cellulose in order to enhance surface interactions between cellulose with high density polyethylene based on the principle "like dissolves like".

Keywords: Gaseous acetylation, microcrystalline cellulose (MCC) , High density polyethylene, Hydrophobicity, Packaging materials.

INTRODUCTION

Cellulose is a biopolymer consisting of D-anhydroglucopyranose Monomeric units linked together by β 1, 4-glycosidic covalent bonds in long chains, linked together in bundles known as microfibrils that can be easily cleaved by mineral acids. Native cellulose is composed of amorphous and crystalline domains. Cellulose nanocrystals are the crystalline portion of

cellulose. The crystalline domains is highly ordered and much more stable to acid hydrolysis treatments compared to their amorphous counterparts [1, 2, 3]. In recent years, there has been an increasing interest from government and customers in new materials from renewable and sustainable resources that are biodegradable, non-petroleum based, carbon neutral, eco-friendly ways to modify such materials, and have low animal / and or human health and safety risks. Native cellulose based materials (wood, hemp, cotton, linen, etc.) have been used as construction materials [4, 5]. Lignocellulosic biomass resources provide a key materials platform for the sustainable production of renewable, recyclable, and environmentally-preferable raw materials for producing goods and products for societal needs in the twenty first century. Wood, is made up of cellulose nanofibers that are extremely strong, has the potentials to replace non-sustainable materials such as plastics and metals. Isolation of nano-dimensional cellulose and its use in nanocomposites will allow the production of much lighter weight materials to replace metals and plastics in various applications. The manufacturers of packaging products, for example, are gradually substituting plastics, glass, and metal packaging materials with paper and paperboard which are far more sustainable and “eco-friendly”. With increasing interests and understanding of the topography and surface chemistry of cellulose, researchers are able to use the basic chemistry of cellulose to control attractive and repulsive forces between wood/lignocellulosic fibers and other materials through modifications to produce materials that are essentially nanodimensional. Most work, to date, has been the result of empirical formulation where wood or pulp fibers are mixed together with other components to make useful functional materials. Cellulose is a material which has unique tensile properties. In its pure form, fibers stronger than Kevlar can be tailored (Cellulose = 70 to 137 GPa, Kevlar = 100 GPa). Other properties of interest that are being achieved with cellulose blends/composites include formability and geometrical complexity at very small scale, unique physical properties, surface smoothness, biomedical compatibility, and ability to reinforce polymer foams. It is also desired through the use of nanomaterials, and chemistry to either form or reform cellulose fibers in a variety of matrixes in which the cellulose can contribute its full modular strength to the matrix. It has been established that cellulose is responsible for the strength of wood. Surface modification plays important roles in the formation of high strength interfaces between the matrix, matrix components, and cellulose for the formation of chemical bridges between the cellulose, the matrix, and other fillers that may be used [6]. Cellulose has a high reactive surface of hydroxyl groups (–OH) sites that facilitates chemical modification to achieve different surface properties (surface functionalization). Cellulose fibrils naturally possess a high surface polarity (hydrophilic) which does not interact well with the hydrophobic surface of the most commonly used synthetic polymers [4, 5]. Studies have been carried out on different methods to achieve better interaction/adhesion between the two phases and to improve the barrier properties of cellulose materials such as chemical modification [7, 8]. With increasing interests particularly for the production of novel materials with nano-scale for eco-friendly industrial applications and considering the important role played by packaging material properties on food safety and quality preservation. A good packaging material should provide control of mass transfer between the food, the packaging material itself and the environment. Different polymers, polymer blends and composites are the most widely used barrier materials in the world today. Microcrystalline cellulose as polymer composite reinforcement is attracting more attention because of its potential advantages such as renewability, biodegradability, good mechanical properties and a broad capacity to allow tailoring or grafting of chemical species (chemical modification) to improve barrier properties [4]. It is therefore, the objective of this study to prepare acetylated

microcrystalline cellulose (AMCC) films with good barrier properties to water sorption for packaging applications. To achieve this, microcrystalline cellulose (MCC) purchased from Aldrich chemicals was chemically modified by ketene in gaseous phase to modify the side chains of cellulose to further enhance interaction. Ketene reacts with the accessible hydroxyl groups ($-OH$) through a mechanism on cellulose molecules and thereby modifies the highly hydrophilic surface to become more hydrophobic which enhances surface interactions with most commonly used synthetic polymers.

General Experimental Procedure: Thin layer chromatography (tlc) plates were studied under the UV-lamp at 256 nm and 366 nm. Infrared Spectra were recorded on a Perkin-ELMER instruments 100X FT-IR run as KBr Pellets disk over the Spectral range to 500 cm^{-1} to 4000 cm^{-1} . 1H and C-13NMR Spectra were recorded on a BRUKER AC 200 MHz Spectrometer using $CDCl_3$.

Reagents and solvents

The microcrystalline cellulose (MCC) cellulose used in this work was purchased from Aldrich chemicals. Acetone, toluene, cyclohexanone, dichloromethane, n-hexane, petroleum ether, diethylether, methanol used were of analytical grade. Metal used include iron filings, zinc granules. Anhydrous Magnesium sulphate was used to dry solutions. Acetone was distilled twice for optimal purity.

Apparatus Description

The apparatus adapted for the generation of ketene is a modification of the conventional apparatus for ketene generation [9, 10], where the electrical chamber was replaced by a thermal chamber. 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 2 mm internal diameter and 3 cm long packing in a Pyrex glass combustion tube than conventional apparatus whose filament is 70 cm long and sealed in a Pyrex glass 25 cm long and 70 mm internal diameter. The novelty in this work is that, the use of metals and thermal chamber provides a shorter 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.

Mercerization of wood cellulose

10 g microcrystalline cellulose (MCC) was weighed into the reaction flask and then 20 % of 20 mL NaOH solution was added the suspension was mechanically stirred for 24 h for ketene uptake and subsequent functionalization of the biopolymer.

Acetylation of microcrystalline cellulose (MCC)

Iron filings-generated ketene

10 g of microcrystalline cellulose (MCC) was mercerized in 20 % of 20 mL NaOH, the suspension was stirred for 24 h on a magnetic stirrer. The suspension was transferred into the reaction flask. The iron pipe adapted as the furnace was packed with iron filings and pre-heated for 10 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 for acetylation. The mixture was

cool to room temperature while stirring with a magnetic stirrer. It was filtered and the residues washed with distilled water until neutral and air dried. The dried residues were ground in a porcelain mortar, sieved through a 2 μm mesh. The fine particles were collected and stored at room temperature prior to IR and NMR analysis. This procedure was repeated for (zinc granules) that were used for the generation of ketene and subsequent acetylation. Acetylation products obtained were assigned codes as shown below:

Table 1. Acetylated microcrystalline cellulose products

KET-CELL
AMCCRF _e
AMCCRZ _n

AMCCRF_e-Acetylated microcrystalline cellulose residue from iron filings generated ketene; AMCCRZ_n-Acetylated microcrystalline cellulose residue from Zinc granule generated ketene

Applications of novel solvent for dissolution of high density polyethylene (HDPE)

High density Polyethylene (HDPE) sachets were collected from the Ibrahim Badamasi Babangida University (IBBUL) main campus. Dissolution of 5 g high density polyethylene sachets follows the method described [11]. Into this clear solutions was introduced 2.5 g of each modified and non-modified samples and stirred for 5 min and then spread on clean metal plates and Petri dish to form a film. The thin films formed were peeled-off to afford modified and non-modified cellulose-polyethylene blends.

Biodegradation studies of modified cellulose blends

Modified and non-modified cellulose-polyethylene blends were subjected to biodegradation studies, using fungal and bacterial test. This was carried out by taking a 6 x 4 cm and 40 μm thickness sheet of blends obtained from novel solvents were buried under the ground with favourable moist condition. The sheets were taking out after 3 months and assessed for biodegradation using their appearance, brittleness, perforation and weight loss parameters.

Water sorption test of modified cellulose-polyethylene blends and controls

Modified cellulose-polyethylene blends and controls measuring 4 cm x 2 cm and 40 μm thickness were prepared and the weight of each sheet was noted. Both blends were soaked in water for 24 h. at room temperature and taking out and allowed to air dry for 1h. and the weight was taken. The procedure was repeated four times and weight determined as average weights. The percentage weight increase due to water absorption was calculated based on the original weight of the air dried blends.

RESULTS AND DISCUSSION

The FT-IR spectra data of treated samples were indicative of the success of the reaction using gaseous ketene. The carbonyl stretching vibrations were observed at 1691 and 1692 and the medium band at 1072 cm^{-1} respectively. The methyl bands (CH_3-) were observed at 29.25 cm^{-1} on the acetylated microcrystalline cellulose (AMCC). The absorption band at 2873.28 cm^{-1} of non-acetylated microcrystalline cellulose (AMCC) has been assigned to C-H stretching vibrations in cellulose and hemicelluloses. After acetylation, this band was observed at 29.25 cm^{-1} . This is due to asymmetric stretching of aliphatic methyl (CH_3-) group which is evidence of

acetylation [12]. The strong absorption bands at 3739.66 and 3316.16 cm^{-1} have been attributed to —OH bonded stretching vibrations in cellulose and hemicelluloses [13]. The presence of these bands in the acetylated sample is attributed to the facts that chemical modification is not always sufficient enough to eliminate all the hydroxyl groups (—OH) [14]. Further evidence of acetylation are the C—O stretching of acetyl group in acetate at 1072 cm^{-1} (medium) [13]. and the absorption band at 1373.78 cm^{-1} (—C—CH_3) 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 [15, 13].

Table 2: IR Spectra band assignments of acetylation products based on related literature [12, 14- 20]

Frequency (cm^{-1})	Assignments
3316.16-3843.09	—OH bonded stretching vibrations
2925	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
1373.78	C—H deformations of CH_3 group in Acetyl
1072	C—O stretching of acetyl group in acetate
1014.40	C—O stretching vibrations in cellulose, hemicelluloses and primary alcohol

The ^1H nmr data are indicative of the presence of six (6) methyl protons of acetyl groups in the range of 1.3-2.4 ppm and the seven (7) cellulose proton absorbance in the range of 3.5-3.9 ppm.

The solvent peak came up at 7.25 ppm as a singlet.

Table 3: ^1H -NMR chemical shifts of acetylated products [17, 18].

Acetylated microcrystalline cellulose (AMCC)		
Chemical shifts [ppm]		
1.4	1.3	1.6
1.6	2.2	2.2
2.2	2.2	2.2
2.2	2.3	2.2
2.2	2.4	2.2
2.3	3.7	3.5
		3.6

Table 4. Assignments for ^{13}C -nmr Signal shifts of acetylated products [12, 14,16- 22]

Acetylated microcrystalline cellulose (AMCC)					
Chemical shifts [ppm]					
ppm	Assignment	ppm	Assignment	ppm	Assignment
29.9	CH_3 of acetyl				
30.19	CH_3 of acetyl	29.9	CH_3 of acetyl	29.9	CH_3 of acetyl
54.59	C6	76.59	C5	76.59	C5
76.59	C5	77.23	C3	77.23	C3
77.23	C3	77.87	C2	77.86	C2
77.87	C2			97.10	C1
128.38	aromatics				



Figure 1. Photographic plate of Acetylated microcrystalline cellulose blend (biodegradable packaging material)

The C-13 nmr peaks of the modified products indicated the presence of an important signal of methyl protons of acetyl groups in the range 29.9-30.2 ppm. The presence of this peak is a strong evidence of acetylation. The cellulose back-bone (C₁, C₂, C₃, C₅ and C₆) revealed by C-13 nmr (Table 4) in the range 54.59-97.10 ppm (97.10 ppm for C₁ due to electronegative oxygen atom) is an indication that, the microcrystalline cellulose that was mercerized and acetylated using gaseous ketene was transformed at morphological level enhancing the uptake of acetylating agent and subsequent functionalization of the accessible hydroxyl groups. This showed that acetylation occurred. The ¹H-nmr analysis of the products indicated a C₄ proton peak at 3.6 ppm. DEPT spectrum analysis (Figure 12a and 12b) gave an additional proof for cellulose back-bone morphology and acetylation by indicating the presence of seven (7) protonated carbons (CH-1, CH-2, CH-3, CH-4, CH-5, H₂C-6a and 6b and CH-7 (CH₃ of acetyl group) which further gave evidence for the structure of the acetylated products. The structure of modified product (Fig. 1) was established based on the evidences provided by spectra data as shown in table 3 and 4 and a DEPT spectrum analysis (Appendix 12a and 12b).

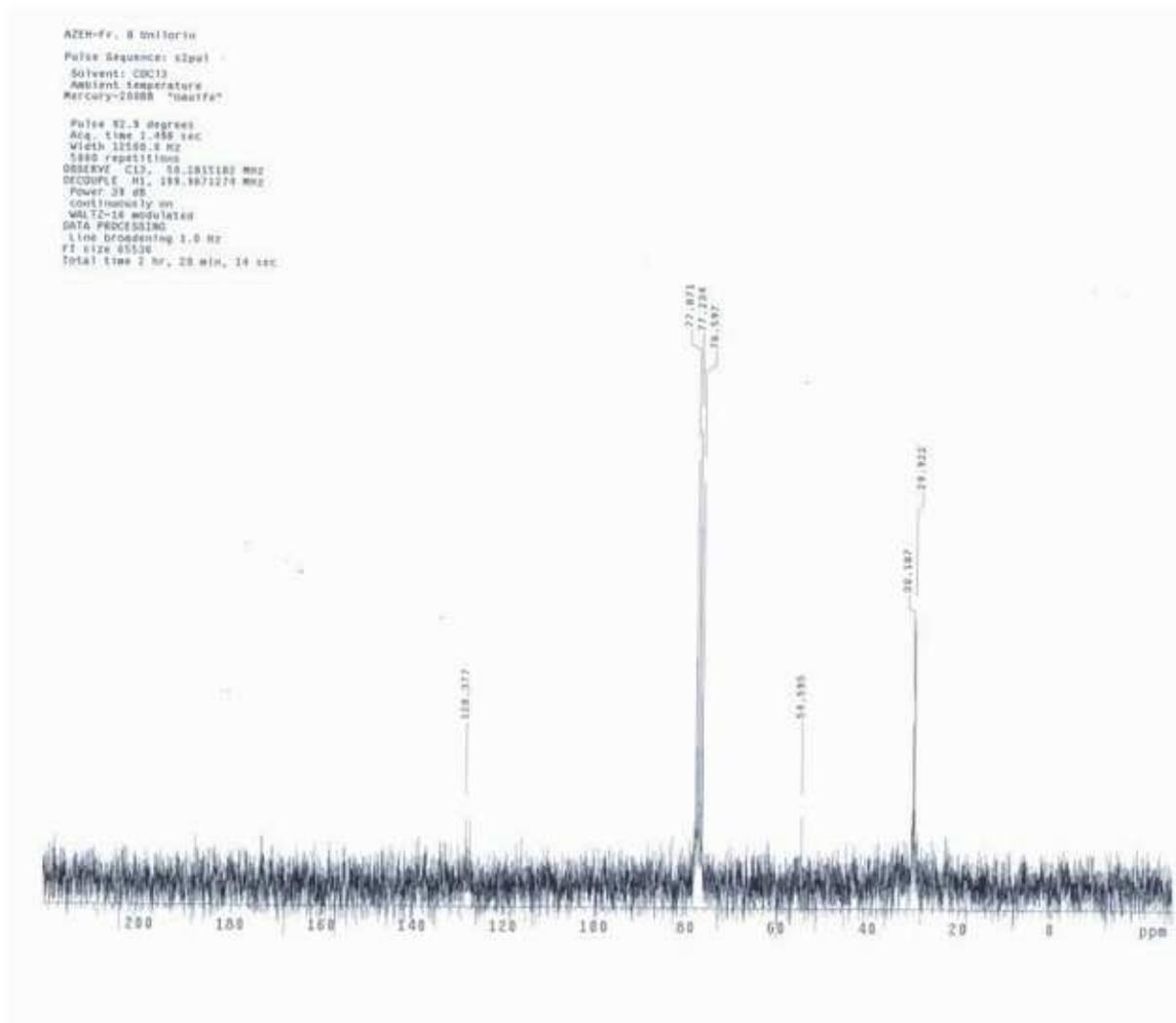


Figure 2. ¹³C- nmr of Acetylated microcrystalline cellulose

ADEPT SPECTRUM ANALYSIS

index	frequency	ppm	intensity
1 D	6438.2	128.030	45.170
2 D	6327.9	125.838	47.530
3 D	6307.7	125.436	52.970
4 D	6023.9	119.792	44.560
5 D	2052.7	40.820	47.530
6 D	2032.1	40.410	57.960
7 D	2010.7	39.985	34.440

Number of protonated carbons: 7

CH : 7
 CH2 : 0
 CH3 : 0

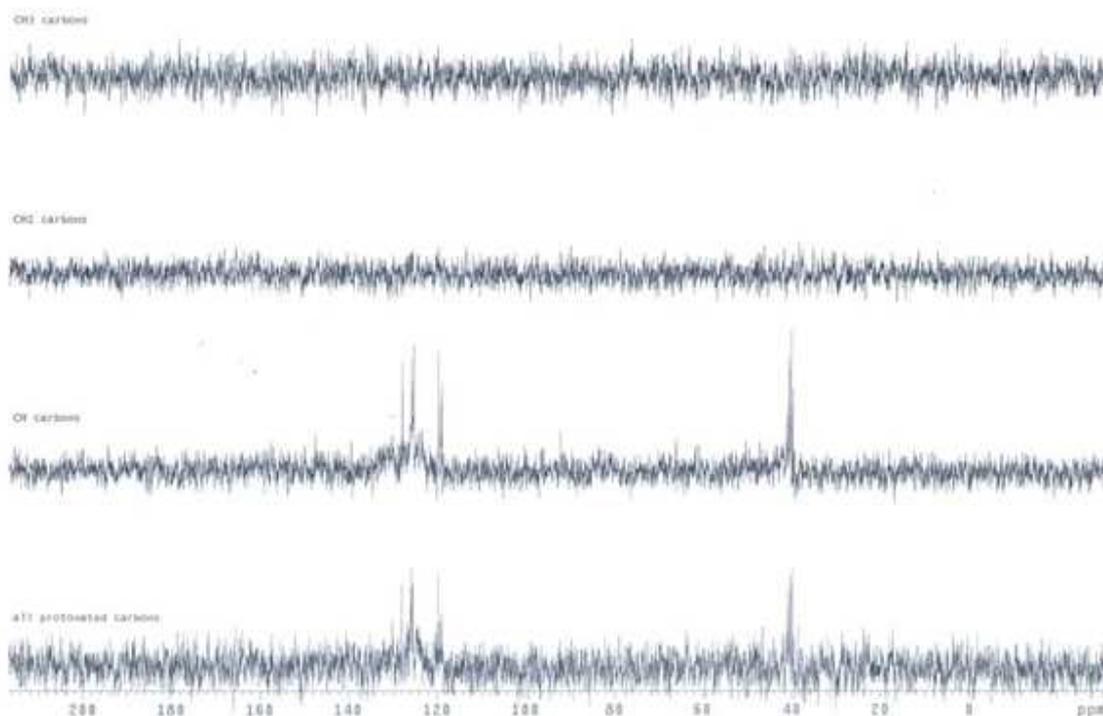


Figure 3. ADEPT Spectrum analysis of Acetylated microcrystalline cellulose

CONCLUSION

FT-IR, $^1\text{H-NMR}$, and C-13 NMR peaks changes observed in 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 by the method adapted was successful. The novelty in this work is that, the use of metals and thermal chamber provides a shorter 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. Also the Acetylated Microcrystalline Cellulose-Polyethylene blends (AMCCPB) prepared showed improved mechanical and chemical properties, for example, they were smooth, transparent, flexible and biodegradable. While control sample did not exhibit such properties. These properties displayed by Acetylated Microcrystalline Cellulose-Polyethylene blends (AMCCPB) is an indication that barrier properties in cellulose that prevent proper interactions with most synthetic polymers have been modified and hence, allowed for processing of blends for packaging applications in food, pharmaceutical, and textile industry.

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