STUDYING THE CHARACTERISTICS OF POLYSTYRENE- MODIFIED COCOA (*Theobroma cacao*) WOOD CELLULOSE ACETATE MEMBRANE

*[1]Okolo, P. O., [2]Adimula, H. A, [3]Osuoji, O. U. and [4]Jideonwo, A.

[1,2,4]Materials Testing Research Centre, Department of Chemistry, University of Benin, Benin City, Nigeria.
[3]Department of Physics, University of Benin, Benin City, Nigeria.
*Correspondence author: okolopao@yahoo.com

ABSTRACT
In this work, cellulose was obtained from cocoa wood (Theobroma cacao) by the chlorite pulping process. The harnessed cellulose was acetylated by the process of step-wise acetylation to a degree of acetylation (DA) of 2.06. Ten percent (10%) solution of the acetylated cellulose material in acetone was used to cast membrane. Polystyrene was used to modify the cellulose acetate and was also used to cast membranes. The modified and unmodified membranes were characterized in terms of their salt rejection capacity, extent of dissolved solid (DS) removal, fold endurance, water permeability, swellability in organic liquids and organic liquid separation potentials. The modification of the cellulose acetate with polystyrene increased its potential for salt rejection by 91.10%, dissolved solid (DS) removal by 98.06, fold endurance by 100%, but decreased its permeability to water by 10%. The result of the permeation test for organic solvents showed a variation in the permeation rate of the organic liquids ranging from 6.08×10^{-4} $molcm^{-2}sec^{-1}$ for hexane, to $9.67 \times 10^{-4} molcm^{-2}sec^{-1}$ for ethanol. Overall, the modification of the cocoa wood cellulose acetate membrane with polystyrene has led to improvement of properties.
Keywords: cellulose acetate, cocoa wood, membrane, modified, polystyrene.

INTRODUCTION

Biopolymers such as cellulose, chitosan, lignin, xylan, and starch occur in great abundance in nature as an integral part of the biosphere. They form a huge store of renewable polymeric materials. These materials which often exist as wastes have been studied and applied in the development of many useful products and in environmental chemistry (Okolo *et al.*, 2012; Chen *et el.*, 1986; Lipson and Spearkman, 1964; Adams and Smith, 1976; Bello-Perez *et al.*, 2000; Groos and Kalra, 2002). Despite these applications, several tons of biopolymers still exist as wastes and continue to litter the environment. Techniques currently employed to deal with some of these wastes, which is largely by burning, further contributes to environmental problems due to the effects of the combustion products such as SOx, NOx, COx, etc (Cunningham and Saigo, 1999). The cellulosic wastes (which are biodegradable) could however be exploited and modified to provide value-added products which could replace conventional synthetic polymers (most of which are nonbiodegradable) and other materials in several fields including oil recovery (Heinrich and Mischnick, 1999), waste water treatment (Yang *et al.*, 1988), cosmetics and food additives or pharmaceutical applications (Wellisch, 1976).

The interest and focus on agricultural waste is expected to continue world wide as chemists continue to devote great effort in searching for more efficient utilization of renewable lignocellulosic materials (Chen *et al.*, 1986). This interest has given rise to the use of corncobs, bean pods, banana stem, coconut fibre, straws (Adebanjo and Frost, 2004; Choi and Cloud,1992; Choi, 1996; Sun *et al.*, 2002; El-Saied *et al.*, 2003; Sun *et al.*, 2004; Meenakashi *et al.*, 2002). The preparation and modification of cellulosic materials from cocoa wood has however not been extensive. Cocoa wood, found in South West Nigeria in large quantity, are mainly discarded after harvest as a waste. This is because the wood has poor mechanical strength and cannot be used as structural support in most buildings. Although used as fuel(fire wood), it is considered that greater value can be added to it if cellulose is harnessed from it. The effective application of cellulose in its native form is limited. Cellulose can be modified by physical and chemical means (Bhattacharya and Misra, 2004) to get new materials with enhanced properties and wider applications. Chemical modifications of cellulose have been achieved by grafting (Guthrie and Tune, 1991; Jideonwo and Adimula 2006), esterification (Adebanjo and Frost, 2004) and etherification (Viera *et al.*, 2002). These modified cellulosic polymers have been applied in various areas of science with improved performances when compared with the unmodified ones. Graft cellulose has been employed in metal ion scavenging (Jideonwo and Adimula, 2006), water treatment (Yang *et al.*, 1988), and viscofiers for enhanced oil recovery (Wermick, 1985). Cellulose acetate is the most widely used for membrane development. Acetate membranes are used in reverse osmosis for water treatment with some setbacks which include poor strength and difficulty in recyclability. Membrane science researchers have continued to look for ways of improving the strength and performance of these cellulose acetate membranes.

The present article therefore aims at producing cellulose from cocoa wood, converting the cellulose to cellulose acetate, reinforcing the cellulose acetate with polystyrene and applying this in the production of membranes whose properties would be compared with those of the unmodified cellulose acetate.

MATERIALS AND METHODS

Cocoa wood (*Theobroma cacao*) was harvested from cocoa farm in Ile-Oluji town in Ondo State of Western Nigeria. The bark was removed and the wood chopped into chips. This was sun-dried for eight weeks. Vegitable oil (King's, Malaysia), waste lubricating oil and flood water were used.

Analar grade of the following chemicals were used: sodium chloride, glacial acetic acid, ferrous ammonium sulphate, sulphuric acid, acetone, nitric acid, chloromethane, propanol, isopropanol, phenol and methanol, all from BDH, England. Others include ferroin indicator, phosphorous pentoxide (Merck, USA), sodium hydroxide (Avondale Laboratories, England), acetic anhydride, potassium dichromate, ethanol, ethyl acetate, and hexane all from Sigma Aldrich, Czech Republic.

All glass wares (previously washed using laboratory grade soap solution, rinsed with deionized water and dried in hot-air oven) were of Pyrex, England; Unicam Atomic Absorption Spectrophotometer model 969 , England); Buck Infrared Spectrophotometer model M500 IR, USA); Hach Turbidometer model 2100 AN Turbid Meter, USA); Sigma centrifuge model 6-15H,Czechoslovakia) and Venticell oven, USA.

Extraction of cellulose from cocoa wood:

The extraction was performed in two stages :removal of fat followed by chlorite pulping.

Removal of fat:

Cocoa wood was collected from a cocoa farm in South-West Nigeria as agricultural wastes, cut into chips and sun-dried. The sun-dried chips were oven-dried at 60°C for 24hr, ground and sieved. The 0.45mm particulate size were collected and used for the preparation of cellulose according to Browning (1963). Ten grams (10.00g) of the pulverized cocoa wood was extracted at 60°C with 1:2 ethanol-benzene mixture for 4hr using a soxhlet extractor. This was followed by a second extraction with 95% ethanol for another 4hr. The resulting material (fat-free sample) was washed at 100°C with distilled water, filtered and air dried for the experiment. Other batches were prepared to produce enough fat-free samples for the experiment.

Chlorite pulping:

The fat-free sample was oven-dried at 60°C for 24hr. Twenty-five grams (25.00g) fat-free sample, pulverized and sieved to obtain 0.45mm particulate size, was added to 800cm^3 of distilled water maintained at 60 °C and containing 3.00cm^3 of glacial acetic acid in a 2.0-L flask. Sodium chlorite (7.50g) was carefully added to the mixture and heated at 80 °C for 4hr. Another portion of 7.50g sodium chlorite and 3.00mL glacial acetic acid were subsequently added to the pulping mixture hourly, for 4hr. The mixture was then cooled, filtered with a millipore sintered glass funnel. The product (raw or native cellulose material or hollocellulose) was washed with distilled water until it was odour-free and neutral to pH, then oven-dried at 60 °C for 24hr. The percentage of hollocellulose recovered (Browning, 1963) was calculated using:

% weight hollocellulose(native cellulose) =
(W_{HC} / W_{FF})x100%,

where W_{HC} = weight of holocellulose and W_{FF} = weight of fat-free sample.

Acetylation of the native cellulose material.

The acetylation of the cellulose material was achieved by the adaptation of the methods developed by (Viera *et al.,* 2002 and Barkalow *et al.,* 1989). The dry native cellulose material (3.03g) was swollen in distilled water for 1hr and excess water pressed out. The swollen cellulose was stirred in 20.00cm^3 of glacial acetic acid for 30 min., excess acid was removed by filtration. The mixture was then transferred to an ice-cold mixture of 20.00cm^3 xylene, 6.00cm^3 acetic anhydride and 20.00cm^3 of concentrated sulphuric acid in a stoppered flask and allowed to stand for 1 min after which it was heated in an oil bath at 55 °C for 6hr with constant stirring. The resultant material was washed with xylene, methanol and distilled water respectively at 60°C and precipitated by differential solubility in dichloromethane/methanol mixture. The precipitated material (acetylated cellulose or cellulose acetate) was washed with 95% ethanol and dried at 60 °C for 24hr. The degree of acetylation was determined using the saponification method (Viera *et al.,* 2002 and Barkalow *et a.l,* 1989) and acetylation confirmed by infrared spectrum using KBr scanning method. Percent acetylation is calculated by the equation:

$$\% \ acetylation = \frac{\left(blank, cm^3\right) - \left(sample, cm^3\right) \times molarity \ (HCl) \times 0.043 \times 100}{sample \ weight}$$

Preparation and modification of cellulose acetate membranes:

Sixteen percent, 16.0%(w/v), solution of polystyrene was made in a chloromethane and acetone mixture (90:10). A separate 10%(w/v) solution of cellulose acetate in acetone was also prepared. Then 3.0cm^3 each of the solutions of the polystyrene and cellulose acetate were mixed together and membrane was cast from it using the method of El-Saied *et al.,* 2003; Jideonwo, 1981). The cellulose acetate solution alone was also used to cast membranes.

Determination of density of the native cellulose:
Ten grams (10.0g) of the oven-dried native cellulose was placed in a polythene bag together with 20.0g standard weight. They were carefully lowered into water in a graduated cylinder. The volume of water displaced was measured. A blank displacement was carried out under the same experimental conditions, without the cellulosic sample. The difference in the volume of water displaced was used to calculate the density as follows:
Density(g/cm^3) = M/V, where M=mass of cellulose and V=volume of water displaced by sample.

Determination of percent α-, β- and γ–cellulose in the native cellulose:
α-Cellulose is the major component of wood cellulose, while β- and γ–cellulose are the minor components. Together, they are called hemicelluloses. The α-cellulose is insoluble in 18%(w/w) aq. NaOH, while β- and γ–celluloses are soluble in this solution. The β-cellulose is insoluble in 10%(w/w) aq. NaOH (Aspinall, 1959; Roberts *et al.*, 1996). The above principles are used in separating α-, β- and γ–celluloses from the hemicelluloses. Two separate portions (1.50g each) of the hemicelluloses (native cellulose) were separately placed into two 250-cm^3 beakers. The first beaker contained 40cm^3 of cold (20±2ºC) 10%(w/w) aq. NaOH, while the second beaker contained 40cm^3 of cold (20±2ºC) 18%(w/w) aq. NaOH. The content of each flask was stirred and allowed to stand for 1h to form slurry. The slurry was then filtered and washed with distilled water to a neutral pH. The residue from the second flask was the α-Cellulose, while that of the first flask was the β – Cellulose. The determination of the soluble fractions was by oxidation with acidified excess 0.4 N K$_2$Cr$_2$O$_7$ followed by back titration of the excess dichromate using 1.0 N ferrous ammonium sulphate using ferroin indicator (Browning, 1963).

Determination of nitrate degree of polymerization of the wood cellulose:
Based on the methods of Hamilton and Mitchell, 1965, 404.00g of phosphorous pentoxide was slowly added to 1000.00g conc. HNO$_3$ and swirled in a 2-L flask placed on an ice-bath. To 100.00g of this cooled(0ºC) nitrating mixture in a weighing bottle was added 1.00g of the dried wood cellulose (free from fats and lignin). This was swirled at 10min intervals and the nitration of the cellulose was allowed to proceed for 60min. The cellulose nitrate obtained was then washed with 300cm^3 of water at room temperature(28ºC) and latter stabilized by boiling in 200cm^3 distilled waster for 5min. The resultant cellulose nitrate was rinsed with absolute methanol and dried in an oven at 50ºC for 2hr, and latter cooled in a desiccator. The dry cellulose nitrate (0.151g) was placed in a plastic bottle and dissolved in 100cm^3 of ethyl acetate with careful shaking for 2hr. An ubhelode viscometer was used to determine the efflux time of the cellulose nitrate solution and the ethyl acetate used as solvent at 25ºC. The relative viscosity, ŋ$_{rel}$, was calculated as follows:
ŋ$_{rel}$ = t/t$_o$; where t and t$_o$ = efflux times(sec) of cellulose nitrate and solvent, respectively.
The degree of nitrate polymerization, DP, is calculated as:
DP = K[ŋ]; where K=75 and ŋ=intrinsic viscosity.
[ŋ] = (ŋ$_{sp}$/C)/1-K^{i}ŋ$_{sp}$; where K^i=0.35, ŋ$_{sp}$=ŋ$_{rel}$-1=specific viscosity and C=conc(g/cm^3) of cellulose nitrate solution.

Characterization of membranes:
Fold endurance test:
In a typical experiment, a piece of membrane of appropriate size (5.02cm^3 ; thickness, 0.5mm) was cut and repeatedly folded and unfolded severally at the same point until it failed by rupture. The number of times the membrane was folded without rupturing gave the value for the fold endurance (Kiyose *et al.*, 1995).

Permeability test:
The membranes were characterized by determining their permeability to water. The permeability of a membrane is an indication of its porosity and is determined from the amount of water that passed through it in an hour under gravity. Distilled water(100cm^3) was passed through 2cm by 2cm supported membranes. The volumes of water that peculated through the polystyrene- modified and unmodified membranes within an hour were recorded as the respective permeability in cm^3/hr (Wermick, 1985).

Swelling test:
The swelling characteristics of the modified and unmodified membranes were studied to determine their suitability for use in water and organic liquids as separation membranes according to the methods of Wermick, 1985. The membranes were soaked for 1h in 30.0cm^3 of different test liquids: methanol, ethanol, propanol, isopropanol, hexane and phenol and their integrity visually examined during test. The liquids were then allowed to permeate through fresh membranes under gravity for 5 minutes. The volume flow was measured using a measuring cylinder.

APPLICATION OF THE MEMBRANE
Separation of oil-hexane mixture by the membranes:
The modified and unmodified cellulose membranes were applied in the separation of organic solvent from vegetable oil. Oil-hexane mixtures:5:25; 10:20 and 15:15 by weight (hexane is usually applied in oil extraction) were prepared and separately allowed to permeate through the membranes for 1 hour. Five grams (5.0g) of each eluted sample(p) were collected and analyzed for its oil content by solvent evaporation method. The amount of oil was determined by weight difference. This was recorded and used to calculate the separation factor (Schutte, 2003; Wermick, 1985):

Separation Factor, $\alpha_{B/A} = \dfrac{\left[X_B/X_A \right]_P}{\left[X_B/X_A \right]_F}$

Where X_B and X_A are mole fractions of the components B(hexane) and A(oil), in the permeated(p) and in the feed(f) mixtures, respectively.

Solute rejection from saline solution by the membrane:

The solute rejection experiment was performed following the method of El-Saied *et al.*(2003). A feed saline solution containing 10,000ppm dissolved solid was prepared by dissolving sodium chloride in distilled water. The saline solution was made to pass under gravity through the membrane on a porous support. The value of salt concentration in the permeate C, was determined by titrating 10cm^3 of the saline solution with 0.0141M silver nitrate solution using potassium chromate as indicator.The amount of sodium chloride (C) was then calculated using:

mg/L, NaCl $= \dfrac{V \times E \times M \times 100}{Vs}$

Where V = volume of titer

M = molarity of silver nitrate

E = equivalent weight of NaCl

Vs = volume of sample used.

The rate transport of water through the membrane was measured in cm^3/cm^2/hr and the amount of solute rejected which is the salt rejection percent was calculated using the equation:

% Salt Rejection $= 100(1 - C/C_o)$

Where C = concentration of salt in permeate solution (ppm).

C_o = concentration of salt in feed solution in (ppm).

Removal of total suspended solids (TSS) using the membrane:

Suspended solids were removed from flood water following the same procedure listed for solute rejection from saline solution (El-Saied *et al.*,2003). In a typical experiment, 50.0cm^3 of flood water obtained from drainage and the amount of the total suspended solids (TSS) in it determined using Hach 2100AN Turbid meter. The flood water was then made to permeate under gravity through the membranes mounted on a wire mesh support to prevent its rupturing. The amount of total suspended solids (TSS) removed by filtration using the membrane was determined by difference. The percent TSS rejection was then calculated from the difference in the initial TSS of the flood water before filtration and the TSS of the flood water after filtration as:

% TSS rejection $= = \dfrac{TSS_i - TSS_t \times 100}{TSS_i}$

Where TSS_i = initial TSS of the flood water before filtration and

TSS_t = TSS of the flood water after filtration

RESULTS AND DISCUSSION

Table1 presents some characteristics of the native cellulose from cocoa wood; it shows that as much as 63.20%(w/w) cellulose of high α-cellulosic content (86.60%) was recovered by the chlorite pulping method of cocoa wood. This yield seems reasonable compared with some other reported sources of cellulose. For example, coniferous wood has 50%(w/w) cellulose, deciduous wood(50%,w/w), cotton wool(94%,w/w), and bagasse(38%,w/w), (Nissan and Hunger, 1965).

The infra red spectra of the acetylated cellulose is presented in Fig.1. The proof of acetylation is demonstrated by the presence of three ester absorption bands in the spectra. The absorption band at 1750cm^{-1} which is due to carbonyl C=O stretching of ester, the band at 1376cm^{-1} which is attributable to the C-H band of acetyl group and the absorption band at 1237cm^{-1} which is due to the C-O stretching of the acetyl group. A close examination of the infra-red spectra shows that there was no absorption in the region 1840-1760cm^{-1} in the spectra of the acetylated cocoa wood cellulose. This is an indication that the acetylated materials were free of unreacted acetic anhydride which absorbs in this region (Adebajo and Frost, 2004). In this work, percent acetylation and degree of acetylation under optimum conditions were found to be 36.66% and 2.06, respectively.

One of the major challenges in the use of cellulose acetate membrane is to ensure its structural integrity at the operating conditions. This consideration often makes it necessary for the membranes to be placed on a porous support such as wire mesh during its use. To overcome this, polystyrene has been blended with the cocoa wood cellulose acetate and its properties investigated. Modifying the cellulose acetate with polystyrene produced a tougher membrane with 100% increase in fold endurance, see Table 2. The modified and toughened membrane thus has a better potential to withstand stress due to pressure differential during use. Modification with polystyrene improved the utility cycle of the membrane making it possible to reuse. Water permeability of a membrane is an indication of its porous nature and is determined from the amount of water that passes through it under gravity in one hour. The permeability under gravity of 20cm^{3}hr^{-1} for the acetylated cellulose (compared with the modified analogue, Table 2) indicated that the membrane was porous, showing that casting acetone solution of the cocoa wood cellulose acetate produced a microporous membrane. It would seem from these that the effect of blending polystyrene on the structure of the cellulose acetate membrane is to produce a denser material with much reduced porosity.The production of porous membrane by the coagulation of cellulose acetate (Jideonwo, 1981) have been reported.

The swelling tests showed that the unmodified membrane gave no noticeable swelling in all the solvents tested (methanol, ethanol, isopropanol, hexane and phenol) during the 1h soaking, while for the modified cellulose, there was swelling and disintegration in the tested solvents during one hour (see Table 2).

One of the areas of utilizing membranes is in their application for the separation of organic solvents from oil (Wermick, 1985;). Hexane is frequently employed in the extraction of vegetable oil from their seeds and must be removed from the oil. The results of the separation of feeds (Hexane/Oil) using the modified and the unmodified membrane are presented in Table 2. The unmodified membrane removed 94% of the hexane from the hexane-oil mixture at the optimum hexane-oil mixture ratio of 1:1, while the modified analogue could not withstand organic solvent.

A salt rejection of 88% was obtained for the cellulose acetate, showing that it is selective, i.e., it allows the passage of water molecules but rejects salt molecules in the solution (Table 2). This suggests that the cellulose acetate membranes may be used for the desalination of water. The result of the salt rejection obtained compares favourably with those reported for other cellulose acetate membranes (El-Saied *et al.*, 2003) which had salt rejection value of between 89.30 and 91.80 percent for acetate membrane obtained from the heterogeneous acetylation of cotton cellulose. The results obtained for the polystyrene modified membrane showed that salt rejection capacity improved from 88.0% for the unmodified membrane to 91.10% when modified. The improvement could be attributed to the increased density of the membrane. A denser membrane means that it contains less voids with reduced pore diameter (Jideonwo, 1981). These have led to reduced permeability and a more thorough filtration. In addition, the smaller pore diameter would lead to a greater exclusion of the larger salt molecules and hence results in enhanced salt rejection capacity.

Table 2 shows that total suspended solid rejection of 97.86 and 98.06 percent were achieved by the unmodified and modified membranes, respectively for treating flood water with an initial suspended solid of 350.00mg/L. The slight variation in the performance of the polystyrene-modified membrane may be due to the same reasons of density and reduction in porosity of the membranes.

Table 1: Some characteristics of the native cellulose obtained from cocoa wood.

Sample	Cellulose Yield %	α Cellulose %	Relative viscosity	Nitrate degree of polymerization	Density	Appearance
Native cellulose obtained from Cocoa wood	63.20 + 0.12	86.60 + 0.31	1.461 + 0.0010	270.91	0.880 + 0.023	Yellowish white

Table 2: Some physical characteristics of unmodified and modified cellulose acetate membranes (surface area and thickness of membrane=5.027cm^2 and 0.5mm, respectively).

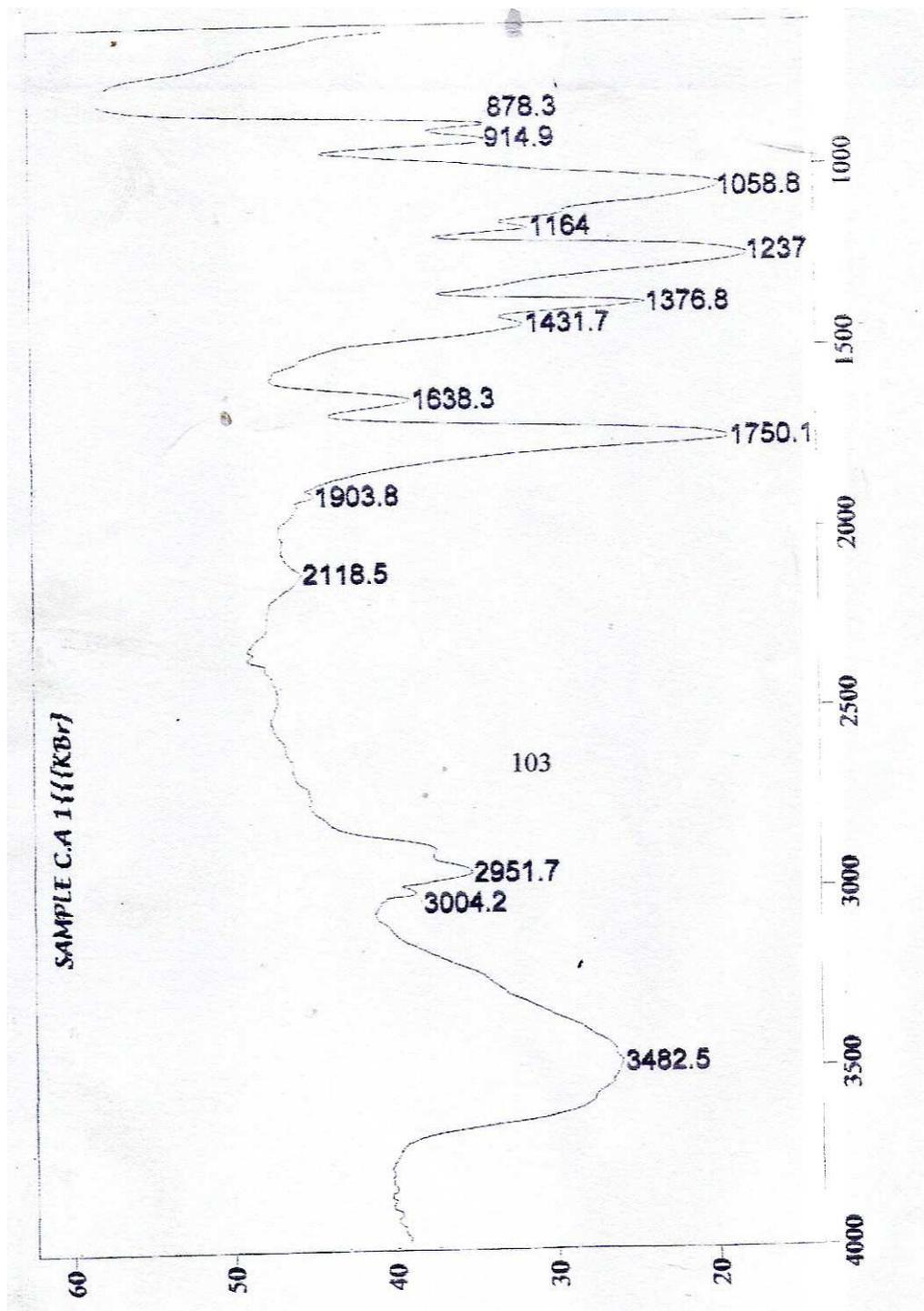| Physical characteristics of cellulose acetate membrane.	Unmodified membrane	Polystyrene-modified membrane
Water permeability(cm^{3}h^{-1}).	20.01±0.65	16.02±0.03
Salt rejection(%).	88.00±0.030	91.10±0.020
Fold endurance.	Membrane ruptured after folding 100 times	Membrane did not rupture even after folding 500 times
Total suspended solids (tss) rejection (%).	97.86±0.20	98.06±0.23
Ability to separate oil-hexane(1:1) mixture (% oil separation).	94.00±0.100	Not applicable, as membrane could not withstand organic solvents
% Acetylation.	36.66±0.10	36.66±0.10
Swilling test.	No noticeable swelling in tested solvents during 1h of soaking	Swelling and disintegration in tested organic solvents during 1h

Fig. 1: The Infra-red Spectra of Cocoa Wood Cellulose Acetate

CONCLUSION
The coagulation of cellulose acetate solution in water produced porous membranes with varieties of characteristics. The modification of the cellulose acetate solution with polystyrene has been used to produce membranes with improved potentials for applications in such areas as removal of total suspended solids and salts from water; only the unmodified analogue was useful in separating solvent (hexane) from its mixture with oil. There was also an improved mechanical strength (as a result of modification) as the material may be used over and over again to a reasonable extent without failure.

REFERENCES

Adams, J.W. and Smith, D.T. (1976). Polymerising in swollen wood pulb fibres. *Appl. Polym. Sci.* **28**, 831-843.

Adebanjo, M.O. and Frost, R.L. (2004). IR and C MASS NMR spectroscopic study of acetylating of cotton. *Spectrochimica Acta.* **60**(2): 449-453.

Aspinall, G.O. (1959). Structural chemistry of the hemicellulose. *Advan. Carbohydrate chem.* 14:429-468.

Barkalow, D.G., Rowell, R.M. and Youg, R.A. (1989). A new approach for the production of cellulose acetate by acetylation of wood pulp with subsequent isolation of cellulose acetate by differential solubility. *J. Polym. Sci.* **37**, 1009-1018.

Bello-Perez, L.A., Cantresas-Ramos, S.M., Jimenez-Apacino, A and Parades-lopez, O. (2000). Acetylation and characterization of Banana *(Musa paradissaca)* starch. *Acetacientifica venezolana,* **51**, 143-199.

Bhattacharya, A. and Misra, B.N. (2004). Grafting: a versatile means to modify polymers. Techniques factors and applications. *Proa. Polym. Sci.* **29**, 767-814.

Browning, B. L. (1963). Methods for the analysis of paper and related products. In handbook of analytical chemistry. Louis Meites edn. McGraw hill Book Coy. Network. Pp13-159 to 13-162.

Chen, R.L., Kokta, B.V., Dareault, C. and Valade. J.L. (1986). Some water soluble copolymers. *J.Appl. Plym. Sci.* **32**, 4815-4826.

Choi, H.M and Cloud, R.M. (1992). Natural sorbent in oil spill clean-up. *Environ. Sci.technical.*26: 772-778.

Choi, H.M.(1996). Cotton and other natural fibres as oil clean-up sorbents *J. Environ. Sci. Health.* **31**:1441-1446.

Cunningham, W.P. and Siago, W.B.(1999). Environmental science: a global concern 5th edn. McGraw Hill, New York. P. 470.

El-Saied, H., Basta, H.A, Barsoum, B.M. and Elberry, M. (2003). Cellulose membranes for reverse osmosis. *Desalination.* **159**: 171-181.

Groos, A.R., and Kalra, B. (2002). Biodegrable polymers for the environment. *Envinn. Science.* **297**: 803-806.

Guthrie, J.T and Tune, P.D. (1991). The preparation, characterization and application of cellulose-MMA graft copolymers. *J. Polym. Sci.* **29**, 1301-1309.

Hamiltion, J..K. and Mitachell, R.L. (1965). Encyclopaedia of polymer science and technology, vol. 3. (Biakales, N..M. edn). .John Wiley and Sons Inc. New York. P. 227.

Heinrich, J and Mischnick, P. (1999). Determination in the substitution pattern in the polymer of chain of ecllulose acetate. J. *Polym. Sci.* **37**:3011-3015.

Jideonwo, A. (1981). The development of small bore arterial prosthesis: PhD. Thesis. University of Manchester, England P.90.

Jideonwo, A. and Adimula, H.A. (2006). The graft copolymerization of acrylamide onto cellulose using enhanced Fe^{2+}/H_2O_2 redox initiator system. J. Appl. Sci.. *Environ. Management.* **10**(3): 151-155.

Kiyose, A., Shinamoto, S., Taniguchi, H., Murakami, K. and Okano, T. (1995). Cellulose acetate with high moldability and process for production thereof. U.S. Patent. 5919920.

Lipson, M. and Spearkman, J. (1964). Use of polymers to immunize wool against acid dyes. *Nature.* **157**: 590.-595

Meenakashi, P., Noorjahan, S.E., Rajini, R., Venkateswarlor, U., Rose, C.R, and Sastry, T.P. (2002). Mechanical and microstructure studies on the modification of cellulose acetate films by blending with polystyrene. *Bull. Mater. Sci.* 25: 30-35.

Nissan, A.H. and Hunger, G.K. Encylopaedia of polymer science and technology, vol. 3 (Biakales, N.M. edn). John Wiley. and Sons Inc. New York.. Pp. 131-215.

Okolo, P.O., Amah, J.E., Dible, E.N. and Uchechukwu, C.E. (accepted Dec. 2012). Palm inflorescence as adsorbent for the removal of some heavy metal ions (Pb^{2+},Co^{2+},Ni^{2+} and Cd^{2+}) from aqueous system. *Biological and Environmental Sciences Journal for the Tropics (BEST)*. In press.

Roberts, M., Reise, M. and Monoper, G. (1996). Biology: principles, and processes, 1st edn. Thomas Nelson and Sons ltd. Ontraio. Pp 130-132.

Schutte, C. F. (2003). The rejection of specific organic compounds by reverse osmoses membranes. *Desalination* **158**: 258-294.

Sun, X.F, Sun, R.C. and Sun, J.X. (2004). Acetylation of sugarcane bagasse using NBS as catalyst under wild reactions for the production of oil spill sorption- active materials. *Bioresour. Technol.* **95** (3): 343-348.

Sun, X.F., Sun, R.C. and Sun, J.X. (2002). Acetylation of rice straw with or without catalyst and its characterization as natural sorbent in oil spill cleanup. *J. Agric. Food Chem.* **50** (22) 6428-6431.

Viera, M.C., Heinz, T., Antonio-Cruz, R. and Mendoza-Martinez, A.M. (2002). Cellulose derivatives from cellulosic materials *Cellulose.* **9**, 203-212.

Wellisch, E. (1976). Estherification of cellulosics without organic solvents. *Appl. Polyn Sci.* **28:** 844-854.

Wermick, D.L. (1985). Preparation of cellulose acetate membrane and its use for polar solvent -oil separation. U.S. Patent 4541972.

Yang, W., Yang, P., and Wang, Y.K. (1988). Modified cellulose acetate flat membranes for desalination. *J. Polym. Science.* **26**:2683-2688.