Asian Journal of Chemistry; Vol. 24, No. 5 (2012), 1938-1940

ASIAN JOURNAL OF CHEMISTRY

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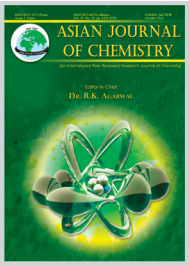

Acetylation of Orange Waste For Possible Industrial Use

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(*Received*: 21 March 2011; *Accepted*: 5 December 2011) AJC-10797

Orange mesocarp were acetylated using acetic acid and acetic anhydride with 0.1 M tetra oxosulfate(vi) acid as catalyst. The acetyation of pure cellulose was carried out in comparison with orange mesocarp. The percentage acetyl content of the products were determined using titration method. The percentage acetyl is higher in cotton cellulose than in orange mesocarp. The infrared spectral of the product was recorded using Perkin-Elmer model 710 B spectrophotometer with KBr disc. The C=O stretch appear at 1757-1630 cm^{-1} for cellulose and 1666-1563 cm^{-1} for orange mesocarp, while the -OH stretch appear around 3600-3100 cm^{-1} for cotton and 3500-3381 cm^{-1} for orange mesocarp. It was concluded that with further work on this research on industrial scale, orange waste could be a good source of raw materials for textile industries.

Key Words: Orange, Acetylation, Waste, Industries, Textile.

INTRODUCTION

Cellulose is a major constituent of cell wall of plants, which provides the backbone structure of plant materials. It is perhaps the most abundant and one of the most useful phyto-chemical compounds on earth. Polysaccharides such as cellulose in its various forms constitute about half of all the polymers consumed industrially in the world[1]. Cellulose acetate (CA) is universally recognized as the most important organic ester of cellulose owing to its extensive applications in fibre plastics and coatings. Acetate fibres of cellulose have lower strength and abrasion resistance than most other man made fibres and are frequently used with nylon on polyester in combination yarns[2]. In recent years, a lot of modifications were carried out on cellulose acetate which enabled its use in pharmaceutical, textile, chemical and leather industries. A reverse osmosis membrane was prepared by graft copolymerizing acrylonitrile onto cellulose acetate[3]. A semi interpenetrating polymer networks containing cellulose acetate, butyrate and poly acryclic ester has been prepared[4]. A cellulose acetate polyurethane blend has been used as ultrafiltration membranes for selectively isolating a mixture of proteins[5]. A super hygroscopic capsule membrane was prepared by encapsulating acrylic acid-starch graft co-polymer using cellulose acetate[6]. Cellulose acetate was prepared from leave vein and stem of banana[7].

Scarcity of raw materials is one of the major problem facing textiles industries in Nigeria. The major raw material is cotton wool (a cellulose), which after treatment with chemicals (acetic acid and acetic anhydride) yields a product forming a textile fibre. The orange mesocarp is cellulosic in composition and up till now it is been disposed as a waste every year.

In the present study, orange mesocarp were acetylated using acetic acid and acetic anhydride. Characterization of the product formed was done by using IR spectrophotometer and compared with acetylated cotton wool.

EXPERIMENTAL

Orange fruits were collected from Sayedero market in Ilaro, Ogun State, Nigeria. It was identified by an expert from College of Plant Science, University of Agriculture Abeokuta, Ogun State, Nigeria. The orange were peeled and inner juicy parts were removed, while the white mesocarp layer were used for the acetylation. The infrared spectral (IR) of the product was recorded using Perkin Elmer model 710B spectrophotometer with KBr disc. All the reagents used are of analytical grade.

Sample treatment: Cellulose acetate was prepared by modifying the method described in previous studies[8]. The dried mesocarp layer of orange was boiled with normal NaOH solution for two hours to remove non-cellulosic materials. It was washed with distilled water to attain the pH of 7.0 and sun dried to get moisture content of about 11-12 %. The material was ground to 100-700 µm size powder in a ceramic mortal. The percentage acetyl in cellulose acetate was determined using titration method[9].

RESULTS AND DISCUSSION

The results of acetylation carried out using different volume of water, which give rise to different temperature changes were shown in Fig. 1. Table-1 shows variation in percentage acetyl at different temperature. The measurements and readings presented were done in triplicates. Figs. 2 and 3 are spectral recorded for orange cellulose and cotton cellulose respectively.

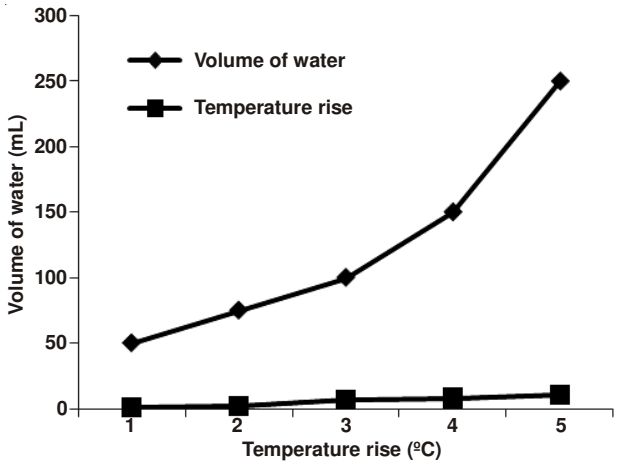

Fig. 1. Temperature rise for various amounts of water with acetic acid and acetic anhydride

TABLE-1
PERCENTAGE ACETYL RECORDED FOR BOTH ORANGE CELLULOSE AND COTTON CELLULOSE AT DIFFERENT TEMPERATURE

Acetyl content of orange cellulose (%)	Acetyl content of cotton cellulose (%)	Temperature of acetylation (ºC)
38.25 ± 02	40.01 ± 01	5 ± 1
32.55 ± 01	38.22 ± 02	10 ± 1
28.12 ± 01	36.85 ± 01	20 ± 1
25.27 ± 01	35.41 ± 02	25 ± 1
24.21 ± 01	30.87 ± 03	30 ± 2

Attempt was made to acetylate orange cellulose after pretreatment with alkali (NaOH). The cotton cellulose was activated by soaking in water to provide a highly active reproducible starting material. It was discovered that using different catalyst such as toluene and perchloric acid the expected results were not obtained. The interaction of acetic anhydride with perchloric acid may form acetyl perchloric acid which is the acetylating reagent but bond formation between the cellulose and the reagents may hinder the acetylation process[10]. Acetylating orange mesocarp with sulphuric acid is faster than acetylating with perchloric acid while acetylating with pure cellulose (cotton) is faster than that of orange mesocarp. This observation is similar to previous works[11]. The mechanism of acetylation with acetic anhydride with acetic acid medium is mainly based on the formation of cellulose sulphate resulting from the reaction of cellulose with sulphuric acid. When the substance formed reacts with cellulose, cellulose acetate is formed and sulphuric acid is set free. The pre acetylation was carried out with various volumes of distilled water as shown in Table-1.

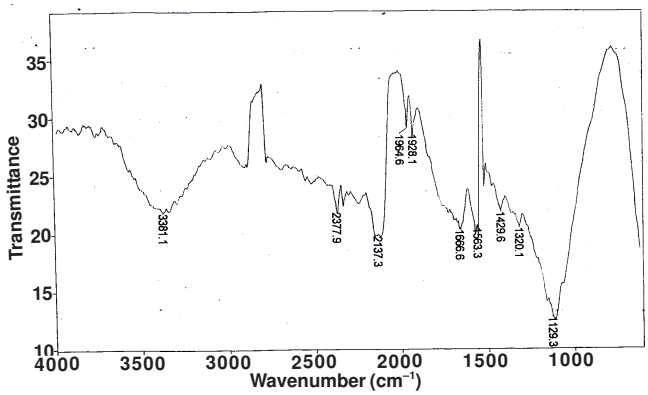

Fig. 2. IR spectra for acetylated orange cellulose

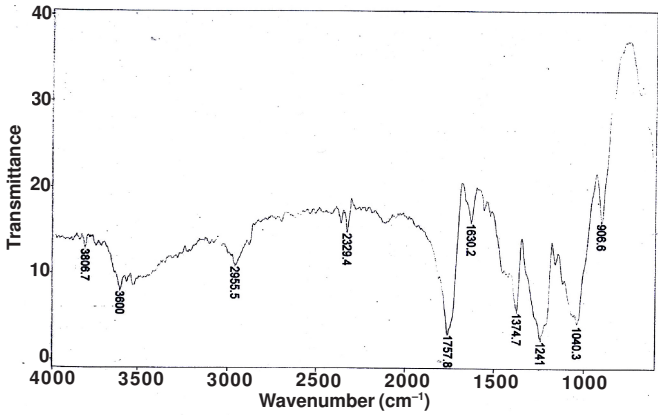

Fig. 3. IR spectral for cotton cellulose

The sulphuric acid liberated can react once again, either with acetic anhydride or with cellulose forming a sulphate[12]. If the reactivity of the substance to be acetylated is good then the rate of second reaction is considerably higher than the first reaction. For this reason, the acetylation mixture contains mainly free sulphuric acid rather than acetylsulphuric acid. Under this conditions, acetylation proceeds primarily through cellulose sulphate. If the reactivity of the substance to be acetylated is poor, then the rate of second reaction is low and slower than the first reaction. For this reason, the sulphuric acid occurs mainly as acetyl sulphuric acid. Under these conditions, acetylation proceeds primarily through cellulose sulphate. The percentage acetyl content of the product was higher in cotton cellulose than orange cellulose as shown in Table-1. The infrared spectra taken for cotton cellulose and orange cellulose were shown in Figs. 2 and 3 respectively. The C=O stretching appear at 1757-1630 cm^{-1} for cotton and 1666-1563 cm^{-1} for orange mesocarp while the -OH stretching appear with strong intensity broad band appear around 3600-3100 cm^{-1} for cotton and 3500-3381 cm^{-1} for orange mesocarp. This is similar to previous work[7]. The C-O stretching vibration bands appear around 1241-1040 cm^{-1} for cotton and 1129 cm^{-1} for orange mesocarp. The C-C stretching vibration band appear at 1630 cm^{-1} on cotton cellulose while it appears at 1563 cm^{-1} on orange cellulose.

Weight increase is due to a balance of water lost and addition of acetyl groups. The degree of substitution and yield increased when the reaction time was extended and the temperature increased[13]. It seems that the diffusion mechanisms play

an important role in making inner OH groups available to the reaction with acetic anhydride. The OH group on the surface of solid cellulose gradually dissolved in the reaction medium and the remaining unreacted OH group will be acetylated subsequently[14]. In addition the high temperature made the swelling ability of cellulose and the diffusion rate of acetic anhydride increase significantly. However, the higher temperature and longer time will result in the hydrolysis of the ester groups and the decomposition of cellulose backbones.

Conclusion

Acetylation of cotton cellulose compared with orange mesocarp was achieved using 0.1 M sulphuric acid as catalyst. The spectral showed that the C=O, O-H, C-O and C-C stretching are very similar to one another. It can be suggested that with further work on this research and some practical trial on industrial scale, orange waste may be a useful raw material for textile industries.

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