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Cellulose Acetate Production from *Acacia mangium* Pulp

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Abstract. One of the main industries with reference to *Acacia mangium* wood utilization is the production of pulp. Apart from yielding papers, pulp has a high potential for cellulose-based product development due to its chemical composition. As for this project, *A. mangium* pulp is developed into cellulose acetate and evaluated based on the effect of time and pretreatment to the degree of substitution of the acetyl group in the polar hydroxyl alcohol groups of cellulose. The cellulose acetate was produced through a series of acetylation process that includes cellulose activation pretreatment, acetylation using acetic anhydride, and hydrolysis. The samples in which was divided into the treated and untreated pulps underwent different acetylation duration; which includes 24, 36, and 48 hours. Results showed that activated samples are more susceptible to chemical modification compared to the inactivated ones due to the homogeneous accessibility of the hydroxyl group provided through the swelling agent, acetic acid. Meanwhile, the optimum duration in obtaining cellulose diacetate was 36 and 48 hours for the activated and inactivated samples, respectively, as longer period of process enables better extension to the hydroxyl group. The income of this study shows the potential of *A. mangium* pulp development as well as denoting the factor affecting the cellulose derivation.

Keywords: Cellulose acetate, *Acacia mangium*, pulp, cellulose

1. Introduction

A leguminous tree from the family of Fabaceae, *Acacia mangium* is one of the most common fast growing species in Sabah, Malaysia. It has garnered many attentions from fellow plantation developer due to its ability to adapt on any type of soil, but mostly on account of its admirable growth rate (Tham, 1976). As the *Acacia mangium* tree can reach up to an increment of 6 meters in height and 15 cm in diameter breast height (DBH) annually, demands for the timber, fibre, and pulp can easily be supplied. However, as bestowed to it the favourable shorter duration of growth, it also inherits the undesirable inferior characteristic of all common fast growing species, in which includes the mediocre density, unstable dimension and susceptibility to pests and diseases. As these previous stated qualities are less suitable for structural applications without technological intervention, one of the alternatives of optimization for *Acacia mangium* wood usage includes the use of fibre for wood composites and pulp production for paper making, in which is famously known for its healthy source of cellulose.

As the cellulose comprises nearly half of the overall chemical composition of *Acacia mangium*, pulp is one of the preferable sources of cellulose as the utilization of rejected or juvenile wood is also viable to produce celluloses. One of the possible derivation of cellulose is the production of cellulose esters, specifically cellulose acetate (CA), in which is a product from the esterification of cellulose with an acetic reagent. The process of acetylation is done by chemically reacting the cellulose, usually from sources such as cottons and wood pulps, with acetic anhydride and sulphuric acid as a catalyst (Steinmeier, 2004). Among the product developments of CA is in textile application such as woven fabrics and home furnishings (Law, 2004), cigarette filters (Rustemeyer, 2004), films (Law *et al*.; Sata *et al*., 2004), and plastics materials (Carollo & Grospietro, 2004).

2. Experimental

2.1. Materials

Acacia mangium pulp was obtained from Sabah Forest Industries Sdn. Bhd. (SFI), Malaysia. Acetic anhydride, sulphuric acid and acetic acid were obtained from Sigma Aldrich. FTIR spectra were obtained using Perkin Elmer Spectrum 100 FTIR Spectrometer.

2.2. Pre-treatment of Wood Pulp

The pre-treatment main purpose is to increase the accessibility of the reagent, acetic anhydride, to all the hydroxyl groups of cellulose. In this project, it includes two stages of the pre-treatment of the pulp samples; the first is the mechanical disintegration, followed by the activation of pulp. For the mechanical pre-treatment, pulp samples underwent a series of mechanical communition to obtain a specifically fit size for acetylation. It is followed by the second pre-treatment that divides the samples into two, the activated and inactivated pulps. Active pulps underwent both mechanical disintegration and cellulose activation, meanwhile the inactive pulp was deprived of the cellulose activation, where 2 g of pulps were soaked in a 20 ml glacial solution of acetic acid to associate with the swelling to obtain a more amorphous structure.

2.3. Acetylation

This process is the main procedure to produce cellulose acetate, as it includes the introduction of the reagent acetic anhydride that enables the acetyl group substitution. The acetylating method is a type of esterification process, which basically substitutes the hydroxyl groups of the cellulose unit to acetyl groups. Acetylation was performed on the active and inactive *Acacia mangium* pulps following methods from Rodrigues Filho et al. (2005) with some modification. 2 g of the pulp samples were mixed with a 30 ml mixture of acetic acid and acetic anhydride, with 0.08 g of sulphuric acid as a catalyst. The samples from each category were then divided again into three (3) categories based on the reaction time length, which includes 36, 48, and 60 hours. The samples were left in room temperature until the predetermined reaction time was up. Distilled water was added to the reaction medium to stop the acetylation process and filtered. The produced cellulose acetate was oven dried for 90 minutes at 105 ^{o}C.

2.4. Hydrolysis

Hydrolysis is the reaction of water that reacts with a chemical compound that involves in splitting of bonds. Similar to acetylation, hydrolysis is actually a reversal of the acetylation process where the sometimes unavoidable over-substitution of hydroxyl group by the acetyl group gives a high degree of substitution, can be repaired. Hydrolysis will help reducing the degree of substitution of cellulose acetate from three acetyl groups per cellulose to the range of 2.4 to 2.5. The reaction involves the use of water as the main reactant (10%) and acids (1%) as catalyst.

2.5. Determination of the degree of substitution

Degree of substitution is the average value of the substituted hydroxyl group in the glucosidic units by the acetyl group. It is one of the most important processes to characterized cellulose acetate. It is determined through a saponification process, where a mixture of 75 ml ethanol and 5 ml nitric acid was mixed into 4 g of pulp samples and stirred for 10-15 minutes. The samples were then boiled for 5 minutes and filtered using warm ethanol. Samples were then oven dried at 70 ^{o}C for 12 hours. 0.7 g of the oven dried samples was mixed with 100 ml sulphuric acid and 25 ml of sodium hydroxide 0.5 N and then heated for 15-30 minutes. The solution was then titrated using hydrochloric acid 0.5 N, with phenolphthalein as indicator.

Equation (1) was used in order to determine the percentage of acetyl groups.

$$DS = \frac{0.162\ A}{(1-0.058\ A)} \quad \text{.....} \quad \text{.....(1)}$$

Where;

A = (BC – DE) / F

B = Volume of sodium hydroxide solution added

C = Normality of sodium hydroxide

D = Volume of hydrochloric acid required for titration

E = Normality of hydrochloric acid

F = Weight of cellulose acetate used

2.6. FTIR

The identification of the end product as well as the infrared spectra was carried out in a Perkin Elmer Spectrum 100 FTIR. Scans were collected for each spectrum with a step size of 4 cm^{-1}. For the analysis, the materials were prepared in the powder form to enable the analysis of the samples.

3. Results and discussion

Approximately 95% of the composition *Acacia mangium* pulp consists of cellulose. The main purpose for this project was to convert the cellulosic component into cellulose acetate. Figure 1, 2, and 3 shows the FTIR spectra of the activated cellulose acetate samples of 36, 48, and 60 hours acetylation, respectively, all with different degree of substitution. Both samples from the 36 and 48 hours shows nearly similar peaks, the opposite meanwhile for the 60 hours samples as the peaks are nearly absolutely different due to the deterioration of samples, resulting from the high acetyl substitution. As for both the spectra of the 36 and 48 hours samples, it overall shows the reduction of OH frequency, as shown in the band 3200 – 3600 cm^{-1} and appearance of C=O band at 1747 cm^{-1}. However, there is a slight trace of hydroxyl group detected even in samples with high degree of substitution (DS) in which was also shown in the band 3200 – 3600 cm^{-1}, indicating that the hydroxyl group not entirely substituted through the acetylation process. There are also little to no traces of acetic acid and acetic anhydride as shown in the absence of band at 1760 – 1840 cm^{-1}. Meanwhile for the spectra of the 60 hours sample, the OH frequency is slightly higher than that of the other samples, with no stretching of the carbonyl group even without any suggestion of the presence of the acetic reagents. This is mainly due to the long acetylation duration time that might deteriorate the overall composition.

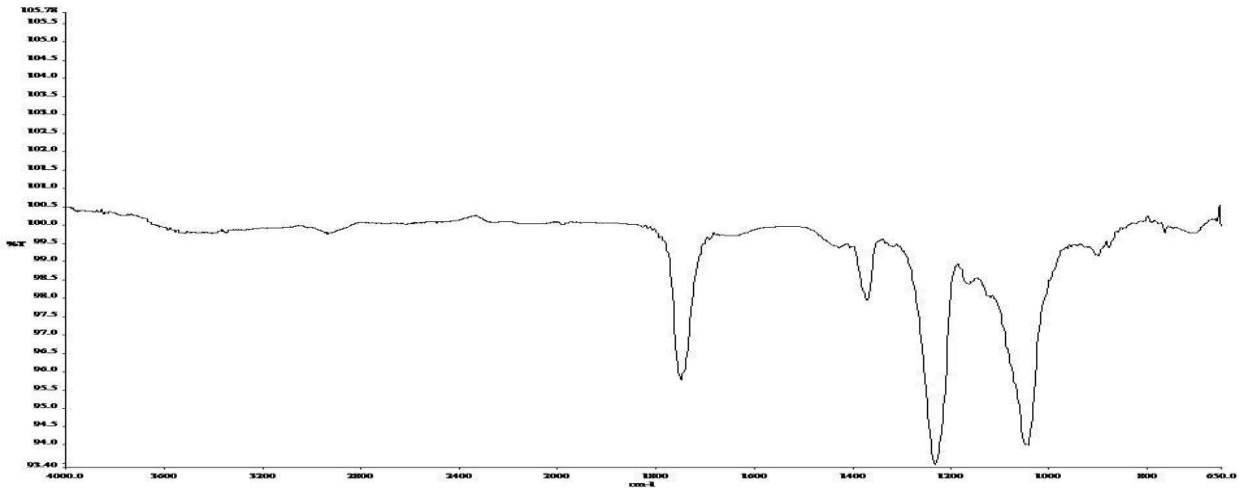

Fig. 1: FTIR of cellulose acetate 36 hours sample

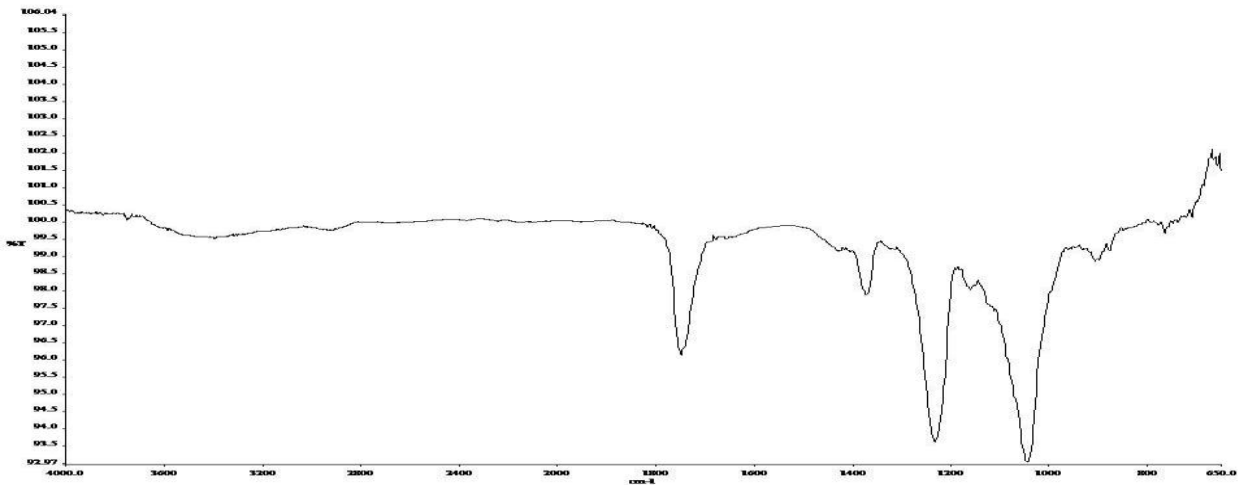

Fig. 2: FTIR of cellulose acetate 36 hours sample

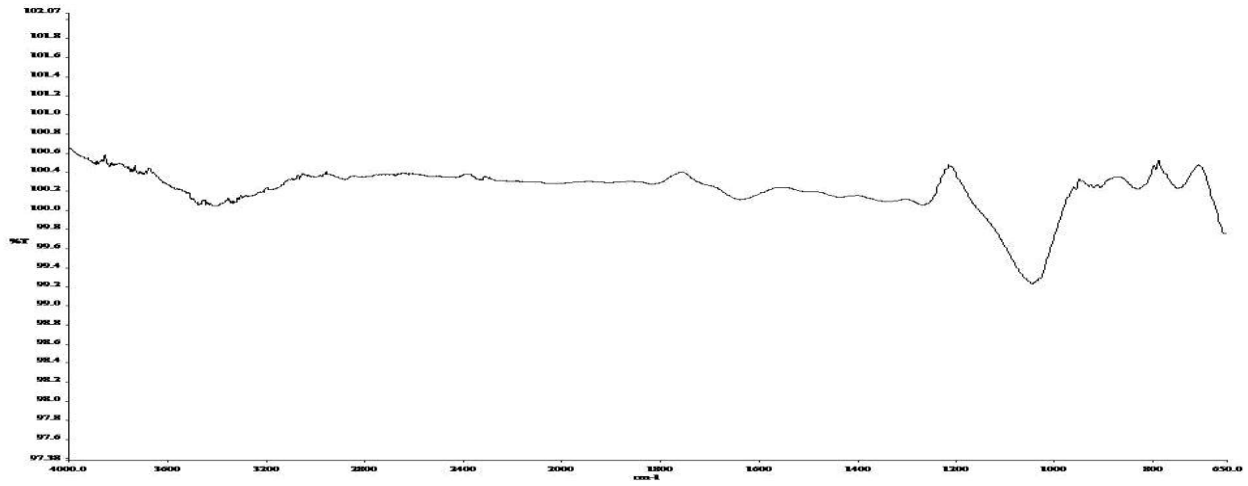

Fig. 3: FTIR of cellulose acetate 36 hours sample

Meanwhile for the degree of substitution (DS), it was determined by titration with aqueous sodium hydroxide solution. Higher DS shows a higher hydroxyl substitution in the monomeric unit by the acetyl group from the reagent. As can be seen in Table 1, DS of samples increases with time, substantially faster for the active samples. However up to a point, the cellulose acetate samples start deteriorating as the reaction has possibly substituted all three of the free hydroxyl group, then targeted the other functional group other than the hydroxyl group.

Table 1: Degree of Substitution of Cellulose Acetates Synthesized in the Laboratory

Active Sample (hour)	DS	Inactive Sample (hour)	DS
36	1.6	36	1.103
48	2.4	48	1.92
60	4.2	60	2.04

4. Conclusion

The cellulose in the *Acacia mangium* pulp samples was converted into cellulose acetate. The conversion rate is low as the reaction duration takes up to 48 hours to obtain cellulose diacetate for the active samples and 60 hours for the inactive samples, without any heat treatment involved. The FTIR spectrum also shows similar peaks for the cellulose acetate, indicating the decreasing hydroxyl group frequency and C=O formation, except for the 60 hours sample as a result to deterioration due to a high degree of substitution. Future production of cellulose acetate from pulp may take other factors such as the size of samples and catalyst concentration into consideration to possibly reduce the reaction time while obtaining the same end product.

5. Acknowledgements

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