Properties of Nitrocellulose from *Acacia mangium*

Melissa Sharmah Gilbert Jesuet, Nurfilzati Munirah Musa, Nurdiana Mohd Idris, Dayang Nur Sakinah Musa and Shirley Marylinda Bakansing

Faculty of Science and Natural Resources, Forestry Complex, Universiti Malaysia Sabah, Jln. UMS, 88400 Kota Kinabalu, Sabah, Malaysia

Email: melissa.gilbert@ums.edu.my

Abstract. Alternatives for petroleum-based products are much needed now due to the depletion of resources and the negative impact of its usage. Amongst the many renewable alternatives of cellulose-based products, nitrocellulose is the oldest and longest thriving derivatives in the world, obtaining a long line of utilization such as biodegradable plastics and film, wood coatings, nail lacquer, automotive paints, and leather finishes. The inexhaustible selection of raw materials for nitrocellulose production are easily obtainable from the copious lignocellulose materials, primarily from cotton and wood pulp. In this study, the *Acacia mangium*, which is a timber species that heavily populates the plantation of Sabah, is used in pulp form to produce nitrocellulose. The objectives of this research was to determine the physical and chemical attributes of the nitrocellulose from two different sizes of *A. mangium* particles (75 and 150 μm), such as its degree of substitution, nitrogen content, rate of efficiency and weight percentage gained. The production method of nitrocellulose includes the nitration process of the *A. mangium* pulp with nitric and sulphuric acid, followed by repeated stabilizing procedures using hot water, and finally extraction process. Among the different sizes, the 75 μm sample showed a lower degree of substitution and nitrogen content compared to the other, but however showed higher rate of efficiency and weight percentage gained. This is due to the higher surface area per volume for the 75 μm samples but which contradicts in DS value due its higher affinity towards absorbing other materials more than the nitrate itself. This was further proven by the infrared and EDX spectra, where the 75 μm sized sample was absorbing more elements but at a lower concentration than the other. This goes to show that samples with a higher surface area per volume does not guarantee a better substitution of nitrate in nitrocellulose production due to the non-specific preference of cellulose absorption.

1. Introduction

*Acacia mangium* is one of the more popular plantation timber species in Sabah, which covers up more than 40,000 hectares of plantation are, which includes FSC-certified plantation such as SAFODA and Sabah Softwood Berhad. It is highly in demand due to its durability towards extreme conditions such as low soil fertility and unfavorable weather condition. Despite its popularity, the utilization potential of *A. mangium* is limited due to its lower density, which ranges from 400 – 480 kg/m3 [1]. The usage of *A. mangium* used to be exclusively for the pulp and paper industry, but has now further evolved into the non-structural utilization such as for moldings and veneers for furniture. Nonetheless, the utilization of *A. mangium* are still limited.

Looking at the utilization of *A. mangium* from a different perspective, chemical-wise, could potentially open up a wide array of product developments from this species. An *A. mangium* wood and pulp fiber could potentially hold up to 43% and 87% of cellulose, respectively, which promisingly could be a great source of cellulose [2]. The unique structure of cellulose enables it to be one of the
more easily modified element, as it is constituted of long chains of glycosidic units with unlimited easily-substituted hydroxyl groups. Dwelling in the cellulose technology potentially opens up a wider development possibilities, specifically in the cellulose derivatives division.

Cellulose derivatives are bio-based materials produced from chemically modifying cellulose. By its very definition, derivatives are imitative materials, wherein related to this research, originally from a natural element and improved through chemical alterations. It is a green alternative for most polymers, as the raw material effortlessly could be obtained from any plants with minimal impact on the environment. Cellulose derivatives could be produced through two processes; etherification and esterification, to obtain the product with enhanced properties [3].

Nitrocellulose is an example of one of the most ancient and still striving cellulose derivatives in the market. It is produced from reacting cellulose with nitric acid to replace the hydroxyl group with nitrate. One of the most prominent characteristics of nitrocellulose is its combustibility, as such, it is one of the main components of gun cottons. Apart from its flammability, nitrocellulose is also soluble in most organic solvents, making it and the other cellulose derivatives a favorite alternative for non-environmental friendly polymer such as polypropylene for product. Product that could be produced from nitrocellulose includes printing inks, wood coatings, nail lacquer, automotive paints, and leather finishes, as well gun cotton and flash papers [4].

2. Experimental

2.1. Sample Preparation

Pure cellulose is a trying source of material to obtain, moreover if it involves the alternative management of biomass waste, where the biomass are instead utilized rather than thrown for nutrient recycling or burnt. Alternatively, *Acacia mangium* was used as the raw material for the production of nitrocellulose in pulp form as it contains over 80% of cellulose. *A. mangium* were obtained from Sabah Forest Industries Sdn. Bhd. The size of the cellulose particle were sieved into 75 and 150 μm.

2.2. Material Preparation

A powerful nitrating agent and a powerful acid is needed to react with cellulose in order to produce a stable nitrocellulose. The reactive mixture is concocted with the combination of nitric acid and sulfuric acid. The weak but potent nitric acid, which contributes the nitrate substitution in cellulose was mixed with the strong sulfuric acid, which acts as the dehydrating agent, to produce the concentrating mixture. The ratio of the mixture is 1:1 of undiluted nitric acid to sulfuric acid, were used to react with cellulose.

2.3. Nitration process

Nitration is the main procedure in producing NC. This process esterifies the cellulose by replacing the hydroxyl group in the cellulose with the nitrate from the main reagent, the nitric acid such as in figure 1 [5]. This process includes the immersion of 2 g of pulp with 94 ml of the acid mix for 90 minutes.

![Figure 1. Nitration of cellulose.](image-url)
2.4. Stabilization
One of the crucial steps in the production of cellulose to prevent sudden combustion due to instability. After undergoing active nitrating process, wet nitrated pulp was immediately immersed in 250 ml hot water (80 °C) to prevent instability. Repeated washings of hot water followed to ensure uniform stability by hydrolysis.

2.5. Dehydration
Extraction was done through dehydration to remove moisture in the nitrated pulp via rotary evaporator. The aim for dehydration is to remove all water and substitute with the appropriate quantity of alcohol to prevent any hygroscopic activity.

2.6. Characterization

2.6.1 Weight Percentage Gained. Weight percentage gained is one of the physical personations of nitrocellulose that comprehends the chemical reaction between cellulose and the reagent, which is primarily the nitric acid. This attribute allows the observation of weight increase from before then after the nitration process finishes. With every increase of weight, it could be evident that some of the reagent has reacted with the substrate, hence forming a new modified material, preliminarily expected to be the nitrocellulose. The method only involves the weighing of the substrate, before and after the full nitration process, following the formula below.

\[
\text{Weight Percentage Gained} = \frac{W_{\text{final}} - W_{\text{initial}}}{W_{\text{initial}}} \times 100\%
\]

Where;
- \(W_{\text{final}}\) = Final Weight of Nitrated Pulp
- \(W_{\text{initial}}\) = Initial Weight of Pulp

2.6.2 Rate of Efficiency. Similar to weigh percentage gained, the rate of reaction shows the rate of reagent absorption by the substrate to allow the calculation of efficiency, instead of weight as per the previous one. The higher the rate of efficiency shows a higher absorption of chemicals that may indicate the quality of the product. However, the residual reagents show the inefficiency of the substrate to absorb or indicates an excessive and unnecessary wastage of reagents. The method involves the weighing of substrate before and after the process, as well as the amount of chemicals used. The formula below allows the calculation of the rate of efficiency.

\[
\text{Rate of Efficiency} = \frac{W_2 - W_1}{C} \times 100\%
\]

Where;
- \(W_1\) = Initial Weight (g)
- \(W_2\) = Final Weight (g)
- \(C\) = Amount of chemical used (g)

2.6.3 Infrared Spectra via Fourier Transform Infrared (FTIR) Spectroscopy. Infrared spectra identification is crucial in identifying the functional group in a sample, in order to identify its element. The chemical investigation of the functional group in the nitrated \textit{A. mangium} pulp were identified using Fourier transform infrared spectroscopy. The infrared spectra was observed by scanning at a cm\(^{-1}\) resolution for transmission wavelength range of 4000 to 400 cm\(^{-1}\).

2.6.4 Elemental Analysis via Energy-Dispersive X-ray (EDX) Spectroscopy. The elemental analysis of a sample is a downright easiest method to identify the element present of a sample. It involves X-ray excitation of the samples. The chemical identification of the functional group in the
nitrated \textit{A. mangium} pulp were identified using an Energy-Dispersive X-ray Spectroscopy. Samples were beforehand coated with gold (Au) to prevent the charging of electrons of the samples.

2.6.5 \textbf{Degree of Substitution}. Degree of substitution is the average value of number of hydroxyl substitution in the monomers in the cellulose. Theoretically, a maximum number of three (3) degree of substitution is allowed per monomer. The degree of substitution was determined through the saponification process that involves the titrating of samples with acid and base.

2.6.6 \textbf{Nitrogen Content}. Nitrogen content were basically obtained through the degree of substitution. For a fully esterified samples with the value of three (3) degree of substitution, the equivalent nitrogen content was 14.1%. Similar to the degree of substitution, the nitrogen content gives information in regard to its proper utilization, with higher nitrogen content traditionally used as ammunition. The nitrogen content could be obtained by using the following formula.

\[
\text{Nitrogen Content} = \frac{3.6 \times \text{nitrogen content (\%)}}{31.13 - \text{nitrogen content (\%)}}
\]

3. \textbf{Results and Discussion}

3.1 \textbf{Absorption Efficacy}

The physical properties included in this research are both in relations with weight increase, which includes the weight percentage gained and rate of efficiency. For both aspects, the main factor for the gaining of weight involves the substitution of hydroxyl group to nitrate, or easily the absorption of the chemicals used to react the substrate with. Providing modification did happen, both samples (75 and 150 μm) does show a promising result, with increments for both aspects. In figure 2, the value of the 75 μm-sized sample for the weight percentage gained is higher than the 150 μm-sized nitrated pulp. Similarly, for the rate of efficiency in figure 3, the efficiency of absorbing the chemicals is higher for the smaller sized pulp. This was due to the higher surface area per volume for the 75 μm-sized sample compared to the other, as well as the hygroscopic nature of cellulose that allows a substantial intake of the reagents. Therefore, in terms of absorption, the 75 μm sized sample showed a better absorption rate than the other, connoting that size does affect the rate of absorption.
3.2 Chemical Characterization. The chemical characterization of the nitrated *A. mangium* pulp involves two methods, which was through functional group identification via FTIR and elemental analysis via EDX. Both procedures have its own advantages, where the EDX is more direct in identifying the elements, the FTIR could show the bonds present in the samples. For the infrared spectra characterization in figure 4, both samples of 75 and 150 μm nitrated *A. mangium* show the appearance of hydroxyl (3415.68; 3392.94 cm⁻¹), nitrile (1634.01; 1634.77 cm⁻¹), amines (1273.25; 1275.01 cm⁻¹), and esters (1067.92; 1055.46 cm⁻¹). However, the 75 μm sized sample has an additional nitro (1541.33 cm⁻¹), alkane (2917.08 cm⁻¹), as well as other organic matter if compared to the 150 μm sample, alluding to the more impressive absorption ability of the smaller sized sample as shown in its absorption efficacy.

![Infrared spectra of nitrated A. mangium (75 & 150 μm).](image)

Meanwhile, the chemical characterization of carbon (C), nitrogen (N), and oxygen (O) were compared between the two samples (figure 5 and figure 6) using the spectra from the EDX. The 150 μm-sized samples exhibit a higher elemental concentration for all three elements, which challenges the proficiency of the 75 μm sized samples greater ability of absorption. Ostensibly due to the non-specific absorption nature of cellulose to uptake other elements apart from the intended nitrate, such a situation was unavoidable. Other foreign presence of elements such as silicon (Si), magnesium (Mg), and gold (Au) was disregarded due to the material of polishing and layering.
3.3 Chemical Substitution

The production of nitrocellulose includes the substitution of hydroxyl group from the carbon in the cellulose with nitrate. The intensity of successful substitution was measured through the degree of substitution, with 3.0 being the highest due to only having three free hydroxyl group in a glucose monomer, in which is interchangeable with the nitrogen content as well. Despite the higher surface area per volume of sample 75 μm, both figure 7 and figure 8 shows that the 150 μm sample has a higher degree of substitution and nitrogen content compared to the former. This further supported the EDX spectra that shows the lower elemental concentration of C, O, and N in the 75 μm sized samples. Furthermore, the IR spectra shows the presence of numerous other elements such as nitro and alkane in the 75 μm samples, which was not present in the 150 μm samples. Albeit the higher absorption amount based on the weight percentage gained and rate of efficiency, the smaller samples allowed the substitution of the eliminated hydroxyl post with other groups, hence accountable for the lower value.
4. Conclusion
The manipulation of size for the *A. mangium* pulp samples for nitrocellulose production was indeed successful in increasing the absorption rate as can be seen in figure 2 and figure 3 for the weight percentage gained and rate of efficiency, where the smaller 75 μm-sized samples has the advantage due to its higher surface area per volume. However, contrary to its absorption efficacy, the smaller samples were seen to absorb or bind numerous other elements during the nitration process that other elements were found presence more than the bigger 150 μm-sized samples such as the nitro groups in thr IR spectra. This was further proven by the EDX spectra, where the 75 μm sized sample was absorbing more elements but at a lower concentration than the other. The degree of substitution and nitrogen content also shows the same pattern of nitration rate, with the bigger sized samples getting the higher value. This goes to show that samples with a higher surface area per volume does not guarantee a better substitution of nitrate in nitrocellulose production due to the non-specific preference of cellulose absorption.

5. References
[1] Sahri M H Ashaari Z Kader R A and Mohmod A L 1998 *Pertanika J. Trop. Agric. Sci.* Physical and Mechanical Properties of *Acacia mangium* and *Acacia auriculiformis* from Different Provenances 21(2) (Malaysia: Universiti Putra Malaysia Press) pp 73-81
[2] Gilbert M S Palle I Liew K C and Salim R M 2013 *Proc. Int. For. Grad. Stud. Conf.* (Kuala Lumpur) Chemical composition of Acacia mangium wood fibre and pulp (Malaysia: Universiti Putra Malaysia Press) 84-86
[3] Shokri J and Adibkia K 2013 *Cellulose: Medical, Pharmaceutical and Electronic Applications* Application of cellulose and cellulose derivatives in pharmaceutical industries (United Kingdom: Intech Open)
[4] Fernandez de la Ossa M A Torre M Barcia-Ruiz C 2012 *Advances in Materials Science Research* Nitrocellulose propellant: characteristics and thermal properties 7 (Spain: Nova Science Publishers) 201-220
[5] Davis T L 1943 The chemistry of powder and explosives 2 (United States: Hauraki Publishing)
[6] Larsson K A and Bavel B V 2015 *Chemical characterisation of nitrocellulose* (Sweden: Orebro University)
[7] Walsh B 1995 Identification of cellulose nitrate and acetate negatives by ftir spectroscopy. *Topics in Photographic Preservation* 6 80-97.
[8] Adekunle I M 2010 Production of Cellulose Nitrate Polymer from Sawdust. E-journal of Chem, (Nigeria: Hindawi) 7(3) 709-716.

[9] Selwitz C M 1988 Research in conservation Cellulose nitrate in conservation (United States: Getty Publications)

[10] Rychly J Lattuati-Derieux A Matisova-Rychla Lyda Csomorova K Janigova I Lavedrine B 2011 Degradation of aged nitrocellulose investigated by thermal analysis and chemiluminescence J. Therm. Anal Calorim, 107 1267–1276

[11] Sharma S K Kumar P Rao R V Sujatha Shukla M 2011 Rational utilization of plantation grown Acacia mangium Willd. J. Ind. Aca. Wood Sc., 8(2) 97–99.

[12] Pourmortazavi S M Hosseini S G Rahimi-Nasrabadi M Hajumirsadeghi S S Momenian H 2009 Effect of nitrate content on thermal decomposition of nitrocellulose. J. Hazardous Material, 162(2-3) 1141-1144

[13] Alinat E Delaunay N Archer X Mallet J M Gareil P 2015 A new method for the determination of the nitrogen content of nitrocellulose based on the molar ratio of nitrite-to-nitrate ions released after alkaline hydrolysis. J. Hazardous Materials, 286 (United States: Elsevier) 92-99

[14] Gilbert M S Palle I 2013 Cellulose acetate production from Acacia mangium pulp. Int. Proc. Chem. Bio. Env. Eng., 58 115-119

[15] Stefke B Windeisen E Schwanninger M Hinterstoisser B 2008 Determination of the weight percentage gain and of the acetyl group content of acetylated wood by means of different infrared spectroscopic methods. Analytical Chemistry, 80(4)

Acknowledgment
This research was supported by Universiti Malaysia Sabah under the SPLB Grant. We would also like to thank our colleagues in Universiti Malaysia Sabah who directly or indirectly provided their insight and expertise that greatly assisted this research.