Synthesis of sodium lignosulfonate from lignin extracted from oil palm empty fruit bunches by acid/alkaline treatment for reinforcement in natural rubber composites

N Thungphotrakul¹, P Dittanet¹, S Loykulnunt², S Tanpichai³, P Parpainainar¹

¹ National Center of Excellence for Petroleum, Petrochemicals and Advance Material, Department of Chemical Engineering, Faculty of Engineering, Kasetsart University, Bangkok 10900, Thailand
² Natural Rubber Focus Unit, National Metal and Materials Technology Center, NSTDA, 111 Paholyothin Rd., Klong 1, Klong Luang, Pathumthani 12120 Thailand
³ Learning Institute and Cellulose and Bio-based Nanomaterials Research Group, King Mongkut’s University of Technology Thonburi, Bangkok, 10140, Thailand

* Corresponding author: fengpwn@ku.ac.th

Abstract. This work studied a synthesis of sodium lignosulfonate (SLS) from the lignin which extracted from oil palm empty fruit bunches (OPEFB) by using batch method. The preparation of lignin from OPEFB was done by acid pretreatment using 1% (wt/wt) H₂SO₄ at 90 °C for 120 min in order to reduce hemicelluloses. Then lignin was extracted by 2.5% (wt/wt) NaOH at 90 °C for 180 min and precipitated by adjusting pH to 2 with 98% H₂SO₄. The obtained lignin was changed to SLS by using sodium bisulfite (NaHSO₃). The study yields of prepared SLS conducted by varying concentration of NaHSO₃. The obtained SLS was characterized by Fourier transform infrared spectroscopy and zeta potential compared to sodium lignosulfonate (commercial).

1. Introduction
Natural rubber is one of important polymers produced in Thailand. Natural rubber has high elastic properties. However, Natural rubber for industrial products has been vulcanized and blended with other biopolymer such as cellulose, lignin and chitosan to improve the properties and sustainable product. In the southern region of Thailand, oil palm industry has an important role in the propel economic in country and that generates large amount of oil palm empty fruit bunches (OPEFB). OPEFB are the biomasses waste from crude palm oil industry and it has molecular structure composed of 30–40 %wt of cellulose, 20–25 %wt hemicellulose and 20–35 %wt of lignin, containing also some quantities of pectin, protein, extractives (nonstructural sugars, nitrogenous material, chlorophyll and waxes) and ash [1]. Base on the study OPEFB, it has about 17.2% of lignin which is high when compared with hardwood and soft wood materials [2]. The isolation of lignin by using direct alkaline treatment is also accompanied by the loss of hemicellulose therefore the biomasses have to be pretreatment with dilute acid to hydrolyze some hemicellulose before alkaline treatment [3]. Lignin is the second most abundant biopolymer next to cellulose. It is a three-dimensional amorphous biopolymer, highly branched. It consists of crosslinked
phenylpropanoid monomer structure, such as p-hydroxyphenyl, guaiacyl and syringyl [4]. The major chemical functional group of lignin are dependent on its genetic origin, and applied extraction processes. The different of chemical function group and network structure of lignin are shown to confer special functional properties such as reinforcing effect, biodegradability, UV-absorption and antimicrobial. Lignin was found unsatisfactory for the reinforcement rubber materials because its difficulty of blending and not being dispersed into the rubber. Sodium lignosulfonate (SLS) is kind of surfactants and product from sulfonation process using sodium bisulfite (NaHSO₃) with lignin starting materials. It has certain degree of surface activity because its hydrophobic hydrocarbon backbone and hydrophilic sulfonic group [5]. The compatibility of SLS with non-rubber components such as phospholipids and fatty acids on natural rubber particles in natural rubber latex becomes good because ionic sites of SLS interacted with the non-rubber components of the surface of NR particles via Coulomb interaction [6]. In this work, lignin was extracted from oil palm empty fruit bunches by acid hydrolysis pretreatment to reduce some hemicellulose in OPEFB followed by alkaline treatment to produce the lignin. The SLS was reaction between lignin and NaHSO₃. The variation of concentration of NaHSO₃ react with lignin, the obtained SLS was investigated by yield of sodium lignosulfonate extraction, Fourier-transformed infrared spectroscopy and Zeta potential.

2. Experiment

Materials: Oil palm empty fruit bunches was supplied from Suksomboon oil refinery 109 Moo 4 Hang Sung, Nong Yai District, Chon Buri 20190. Sodium hydroxide (NaOH) was purchased from Ajax Finechem. 98% sulfuric acid (H₂SO₄) was purchased from Merck in Germany. Sodium bisulfite (NaHSO₃) was purchased from Himedia laboratories Pvt. ltd. Methanol was purchased from RCI Labscan Limited and sodium lignosulfonate (commercial) was purchased from Tokyo chemical industry co., ltd.

2.1 Acid hydrolysis pretreatment

Acid hydrolysis pretreatment for lignin extraction. The oil palm empty fruit bunches (OPEFB) was dried in oven at 65°C for 48 h and reduced size by mill. The acid hydrolysis of OPEFB were weighed into a flask with volume ratio represents in terms of mass percentage: 10%, 89% and 1 wt.% of EFB, water and conc. sulfuric acid (H₂SO₄) respectively stirred at 90°C for 120 min of reaction time. The acid treated EFB was washed three times with DI water and dried overnight at 65°C.

2.2 Alkaline treatment

Alkaline treatment for lignin extraction. Acid treated OPEFB was added into the mixture 2.5% (w/w) sodium hydroxide (NaOH) solution (solid: liquid ratio; 1: 10, w/w) and then stirred at a temperature of 90°C with a time of 80 min. The result solution contains solid is mainly cellulose and hemicellulose, while liquid fraction is rich lignin (black liquor). The separation of lignin in liquid fraction by acidifying adjusted to pH 2 by adding 98% (w/w) H₂SO₄ gradually. The participated lignin was filtered, washed with water for several times then, dried at 35°C for 8 h.

2.3 Synthesis sodium lignosulfonate from extracted lignin

Synthesis of SLS was reaction between 2 grams of lignin and NaHSO₃ solution. The concentration of NaHSO₃ were variation of 0.1, 0.3 and 0.5 M, respectively. The condition of process is constant temperature 90°C and constant reaction time 4 h. SLS liquid phase was evaporated at 100°C then mixed with methanol to precipitate an insoluble bisulfite and filtered. The SLS filtered was evaporated to concentrate the SLS then dried at 65°C to constant weight and the SLS obtained to find the yield analyzed determined by mass balance [1].

2.4 Characterization
Fourier transform infrared spectroscopy (FT-IR) analysis. FT-IR analysis was carried out using a Spectrum 400 FT-IR spectrometer. The spectral range was 4000-400 cm⁻¹. Zeta potential was carried out using a Malvern Nano-ZS90 zetasizer after appropriate dilution of solution using water.

3. Results and discussion

3.1 The yield of sodium lignosulfonate extraction
The yield is parameter to determine the SLS produce from lignin with NaHSO₃. The result of SLS produce with variation of concentration of NaHSO₃ solution show in table 1. By constant the weight of lignin is 2 grams with temperature and reaction time are constant. The results showed the yield tends to increase along with the increase concentration of NaHSO₃. The addition of concentration of NaHSO₃ provide the more interaction between lignin and NaHSO₃ and yielded more SLS.

| Concentration of NaHSO₃ (M) | Temperature (°C) | Reaction time (hours) | % Yield (w/w) |
|----------------------------|------------------|-----------------------|---------------|
| 0.1                        | 90               | 4                     | 37.71         |
| 0.3                        | 90               | 4                     | 48.73         |
| 0.5                        | 90               | 4                     | 51.87         |

3.2 Fourier-transformed infrared spectroscopy (FT-IR)
The FT-IR spectroscopy was investigated function group of lignin and sodium lignosulfonate to confirm the lignin was still remain when it through the acid hydrolysis pretreatment and sulfonate group in lignin structure when added the different concentration of NaHSO₃ by compare with commercial sodium lignosulfonate. The results from FT-IR image of lignin extraction after through the acid hydrolysis pretreatment is show in figure 1a. Lignin was still remaining in sample. The band nearly in 3400 cm⁻¹ are assigned to OH group in aliphatic and aromatic structure. The couple peak between 2920 cm⁻¹ and 2850 cm⁻¹ are characteristic of C-H bonds of CH₂ and CH₃ of propyl side chain and the peak from 1100 cm⁻¹ to 1260 cm⁻¹ to represent the syringyl units. The FT-IR images of prepared SLS with variation of concentration of NaHSO₃ compared with commercial SLS is show in figure 1b. the bands at 1048 cm⁻¹ and 624 cm⁻¹ were assigned to adsorption and deformation of sulfonate group, respectively [7].
Figure 1. FTIR spectra image of OPEFB after acid hydrolysis and lignin (a) and SLS variation of concentration of NaHSO₃ (b).

3.3 Zeta potential
The zeta-potential values, in particular, demonstrate well the electronic charge character of the particles that is inherent to the functional groups of the polymer [8]. The results of lignin and sodium lignosulfonate are negative charged show in Table 2. The addition of NaHSO₃ in lignin was influence increase the negative charge but when increase the concentration of NaHSO₃ influence the trend of negative charge was decrease because may be the high of concentration of NaHSO₃ provide the more Na⁺ in SLS solution.

| Sample                       | Zeta potential (mV) |
|------------------------------|---------------------|
| lignin                       | -53.57              |
| SLS from commercial         | -55.17              |
| SLS from 0.1M of NaHSO₃     | -65.00              |
| SLS from 0.3M of NaHSO₃     | -60.30              |
| SLS from 0.5M of NaHSO₃     | -45.47              |

4. Conclusion
In this work study the synthesis of sodium lignosulfonate from lignin extracted by the sequential acid/alkaline treatment of OPEFB with variation of concentration of NaHSO₃ to investigate the trend of yield of synthesis SLS, structure and functional group in synthesis SLS was analyzed by FT-IR and physical distribution of SLS in the solution was analyzed by zeta potential. So that SLS will be use as reinforcing agent and antimicrobial agent in natural rubber composites for further study and maybe it will be use as dispersants to the counter ion for the filler in natural rubber.

5. References
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