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Sorption of oil emulsified in water on oil palm fibers

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Abstract−Oil palm empty fruit bunch (OPEFB) fibers were modified with silylation by trimethylchlorosilane (TMCS) and diethyldichlorosilane (DEDCS). The investigation was carried out at room temperature at a concentration of 1, 3, 5, and 9%wt and aging time of 3, 5, and 9 hr. Fiber modification was conducted by leaching out surface contaminants resulting in open porous surface. An optimal condition to reach the equilibrium silylation reaction was undertaken at a concentration of 1%wt and aging time of 3 hr. The sorption of oil which was emulsified in water on fresh and silylated OPEFB fibers fit Temkin and Langmuir isotherms, respectively.

Key words: Oil Sorption, Oil Palm Empty Fruit Bunch Fibers, Silylation

INTRODUCTION

The effluent from fish-shrimp processing and palm oil industrial is mainly oily wastes. Oil in contaminated wastes mostly exists in small dispersed droplets that are difficult to recover and degrade the performance of a purification plant, leading to more severe impact. Adsorption has been recommended as one of the promising techniques to reduce such concentration before flowing to the treatment plant [Deschamps, 2003]. Many researches have revealed the performance of sorbent characteristics and reported the development of the adsorption procedure both through adsorbents and other processes. Synthetic products, such as polypropylene, polyethylene and polyurethane, are widely used as adsorbents in the removal of oil from an emulsion. However, these materials are expensive and slowly degradable. Biomass could thus be an alternative and economical material for oil removal from oil emulsified in water [Ahmad et al., 2005; Ribeiro et al., 2000].

Oil palm is one of the important economic plants of Thailand and the plantation area has been increased every year. For every ton of fresh fruit bunch (FFB), approximately 0.28 tons of empty fruit bunch (EFB) remains as solid waste [Prasertsan, 1996]. EFB has been utilized for several purposes including agricultural activities and combustible fuel for boilers. However, more than 60% of EFB still remains unused. OPEFB fibers, natural fibers, composed of lignocellulose material consisting of cellulose, hemicellulose, and lignin, usually account for 65-70% of the plant dry weight basis, which are major components of plant fiber [Han and Rowell, 1997]. These compositions are hydrophilic, namely rich in hydroxyl groups, which are responsible for moisture sorption through hydrogen bonding. The hydrophilic properties must be modified before being utilized for oil removal. Several techniques of hydrophobicity enhancement, such as acetylation, mercerization, and silylation, have been presented. Recently, a few works on hydrophobicity enhancement by silylation on EFB fibers have been disclosed.

EFB fibers have been widely studied as an additive for a composite material. It was found that modification with silylation would strengthen material by less water adsorption [Sreekala et al., 1997; Sreekala and Thomas, 2003; Wang, 2004]. In this study, attempts to enhance EFB for nonpolar compound sorption by silylation were made. Its chemical characteristics and structural images were used to verify the results. Eventually, comparative adsorptions over emulsion and adsorption isotherms were also presented.

EXPERIMENTAL

Oil palm empty fruit bunch (OPEFB) fibers were obtained from a local palm mill, Univanich Palm Oil Co., Ltd. (Krabi, Thailand). Trimethylchlorosilane (TMCS) and Diethyldichlorosilane (DEDCS) were used as silylating agents while NaOH was used as a mercerizing agent.

1. Preparation of Adsorbents

OPEFB fibers were dried at 60 °C over night. Afterwards, they were pre-treated with mercerization by dipping in 5%NaOH at room temperature for 48 hr. The fibers were then washed with distilled water until the washing solution was neutral. The fibers were dried again at 60 °C. Next, the fibers were then modified by silylation by dipping in concentrated silylating agents either TMCS or DEDCS in toluene at room temperature. The concentration of silylating agent of 1, 3, 5 and 9%wt and aging time of 3, 5 and 9 hr was used for the investigation. After the reaction, silane treated fibers were washed with toluene and dried in an oven at 60 °C overnight and kept in a desiccator.

2. Characterizations

SEM photographs of both untreated and treated OPEFB fiber surfaces were taken with a Scanning Electron Microscope (SEM, JEOL JSM-6400). Functional groups on OPEFB fibers were confirmed by Fourier Transform Infrared Spectroscopy (FTIR, Perkin Elmer FTIR-2000).

3. Adsorption Tests

A certain weight of untreated and silylated fibers (selected sample at optimum condition) was cut into 2-3 cm. These fibers were

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dipped in oil/water emulsion at room temperature. The initial oil concentration was varied between 1 and 10 g/*l*. After overnight adsorption, fiber sample was removed. The residual oil content in water was analyzed following standard methods of water quality [APHA, AWWA, WPCF, 1992]. The amount of oil adsorbed by the fiber was calculated by the difference between quantity of initial oil and quantity of oil after n-hexane extraction. Each test run was triplicated for the mean value.

RESULTS AND DISCUSSION

The major chemical components of fibers are cellulose, hemicellulose and lignin. The functional groups, including-OH, -CH, $-CH_2OH$, are ready to react for surface modification. The chemical reactions that take place during treatments by mercerization and silylation are as follows:

$$\text{Fiber-OH}+\text{NaOH}\rightarrow\text{Fiber-O}^{-}\text{Na}^{+}+\text{H}_2\text{O} \tag{1}$$

$$\text{Fiber-O}^{-}\text{Na}^{+}+\text{R}_x\text{-Si-Cl}_y\rightarrow\text{Fiber-O-Si(R}_x\text{Cl}_{y-1})+\text{NaCl} \tag{2}$$

The fiber surface modifications in chemical ways remove natural and artificial impurities that improve fiber-matrix adhesion. The effects of concentration and aging time are discussed.

1. Characterizations by FTIR and SEM

Fig. 1 presents FTIR spectra of both untreated and treated fibers. For instance, the FTIR spectrum of the untreated fiber sample (spectrum a) displays peaks at 925, 1,000-1,735, 2,850, 2,935, and 3,400 cm^{-1}, corresponding to aliphatic OH, phenolic OH, C=O, COOH, CHO, C-C, OCH_3, CH_3, major components of cellulose, hemicellulose and lignin on fibers. More specific, peaks at 1,251, 1,735, 3,000-3,600 cm^{-1}, correspond to COH stretching, C=O stretching and CH, CH_3, H-bonded, OH stretching vibrations. These results agree with structures of EFB, reported by Han and Rowell [1997], Durig et al. [1988], Pandy and Pitman [2003] and Noguchi [2001].

Fibers were modified by in site mercerization (NaOH) prior to silylation reaction with TMCS and DEDCS. Their FTIR spectra are presented in Fig. 1 (spectra b-d). It is difficult to identify the changes after the modifications, since substituted functional groups

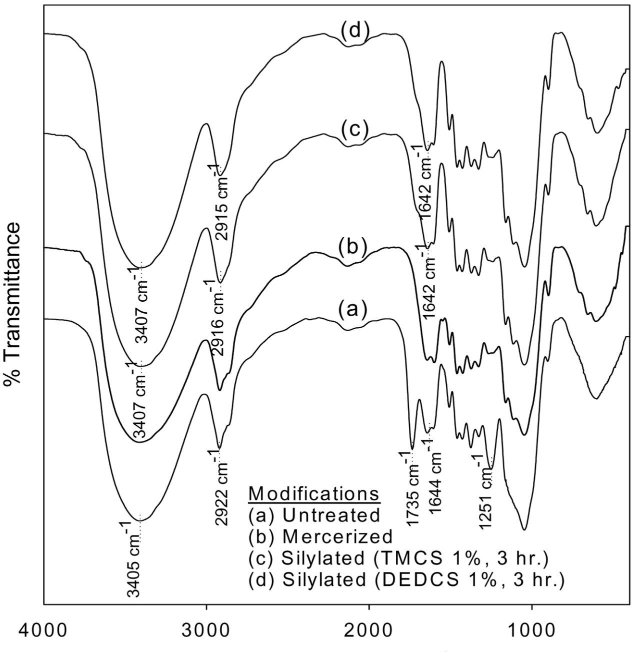

Fig. 1. IR spectra of treated and untreated oil palm empty fruit bunch fibers.

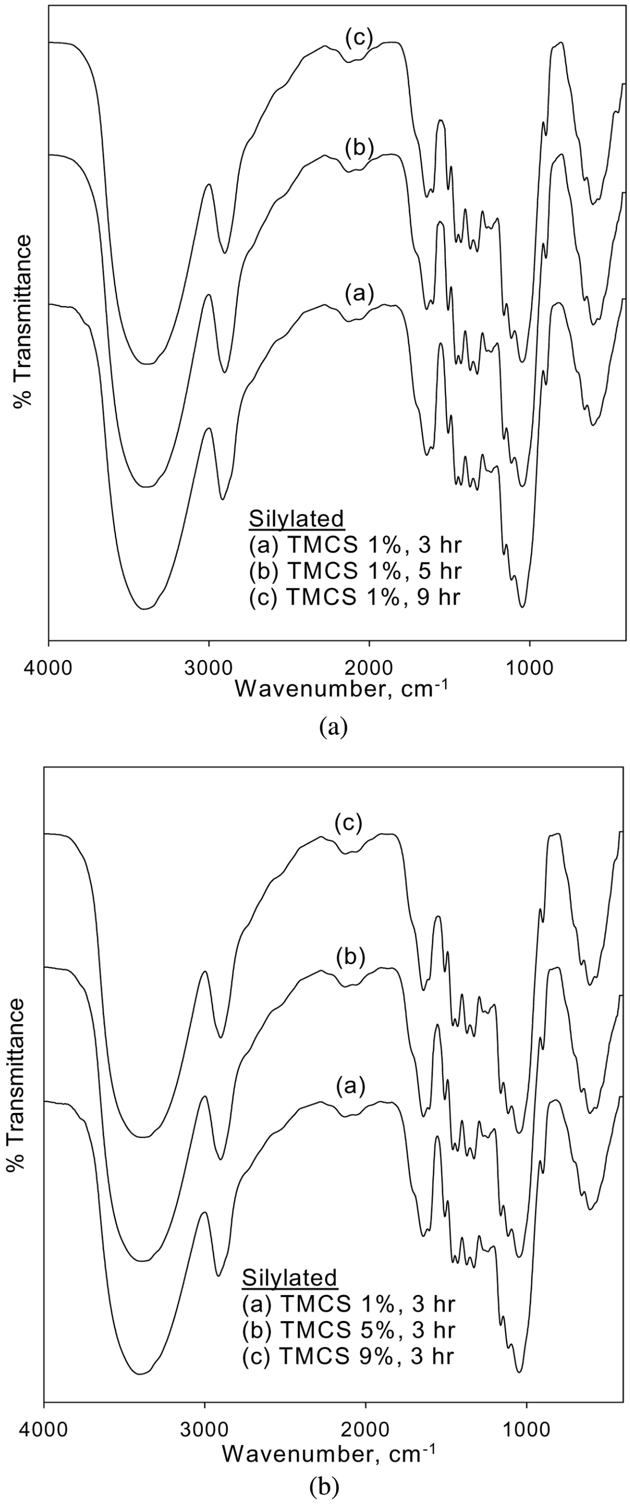

Fig. 2. IR spectra of silylated fibers at different (a) aging times and (b) concentrations.

of Si-Cl$_x$, Si-CH$_3$, Si-O, Si-OH, SiO-H are present mostly in similar wavelengths to those of cellulose, hemicellulose, and lignin. However, there is an absence of a peak at 1,735 cm^{-1} which might due to the leaching out of carboxylic group during the mercerization over the surface by NaOH. Meanwhile, COH stretching at 1,251 cm^{-1} disappeared, due to the substitution of O-Si((R)$_x$Cl$_{3-x}$) by silylating agents and was replaced by the peaks of Si-Cl, SiCl$_x$ at 625 (broad vibrational feature), 710 (stretching mode), 1,100 and 1,150 cm^{-1}, instead [Ferguson et al., 2000; Bu et al., 2000]. More peaks appear around 750 and 850 cm^{-1} corresponding to Si-C, and Si-CH$_3$, respectively. However, peaks for SiO-H both stretching and bending modes and Si-OH could not be seen since they are present at the same wavelength of -OH. The absence of -OH functional group would indicate an increase of fiber hydrophobicity.

Considering spectra silylated by TMCS (Fig. 1c) and DEDCS (Fig. 1d) at the same concentration and aging time of 1% 3 hr, there were not found any differences in these two spectra by different silylating agents. This might due to the limitation of sodium ion occupied after its mercerization, previously. Fig. 2 shows (a) spectra treated by 1%wt TMCS at various aging times (3, 5 and 9 hr), and (b) spectra treated at the same aging time of 3 hr with various concentrations of 1, 5, and 9%wt TMCS. There were no differences visually in all spectra affected by aging times and concentrations. Fibers treated by 1%wt and 3 hr were then used to represent in our further adsorption study.

Figs. 3 and 4 show SEM images, in different magnifications of 200×, 1,000×, and 5,000×, employed to show the development of modifications of untreated and treated fibers. The images of OPEFB fibers presented stomata, microscopic pores in the epidermal tissue, which were spread over the fiber surface. Stomata were removed after being modified by mercerization and silylation. The structure became openly porous. It was believed that higher surface area would afford more adsorption after these surface treatments. The pores were found to have an average diameter of 10, 21 μm, for mercerization and silylation, respectively. A porous morphology has been reported to be useful for better mechanical interlocking with the matrix resin for composite fabrication [Sreekala et al., 1997].

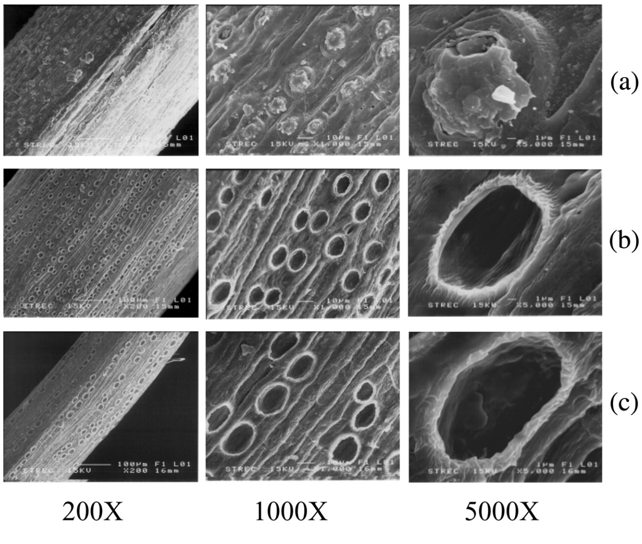

Fig. 3. Scanning electron micrographs of untreated and treated oil palm empty fruit bunch fiber surface (200×, 1,000× and 5,000×) (a) untreated fiber, (b) mercerized fiber, (c) silylated fiber by 1%TMCS, 3 hr.

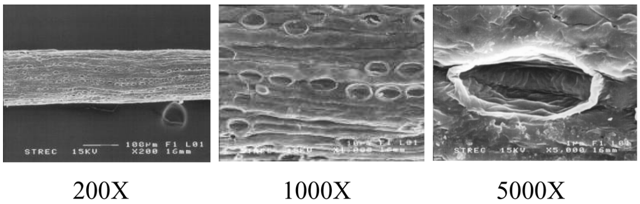

Fig. 4. Scanning electron micrographs of silylated fiber surface by 1%DEDCS, 3 hr (200×, 1,000× and 5,000×).

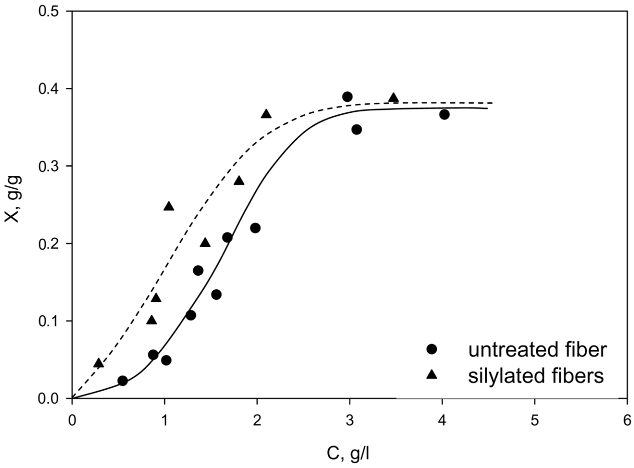

Fig. 5. Adsorption isotherms for the system oil emulsified in water on OPEFB fibers.

2. Adsorption Study for Oil Emulsified in Water

The oil sorption isotherms of untreated and treated fiber in water are given in Fig. 5. The adsorption amount increases with equilibrium concentration at low concentration and reaches a constant at an equilibrium concentration of 3 and 2 g/*l* for fresh and treated fiber, respectively. This indicates that modified fiber could be improved its oil sorption at low oil concentration better than untreated fiber.

Three isotherm equations--Langmuir, Freundlich, and Temkin--are used to describe the experimental adsorption isotherm [Yu and Kaewsarn, 1999]. The Langmuir isotherm is most widely used for the sorption of a pollutant from a liquid solution assuming that the sorption takes place at specific homogenous sites within the adsorbent. The Freundlich isotherm applies as sorption energy exponentially decreases on the completion of the sorption centers of an adsorbent, while the Temkin isotherm assumes that the heat of sorption is rather linear than logarithmic. These isotherms are employed by the following equations:

$$\text{Langmuir equation: } X=\frac{XmKC}{1+KC} \tag{3}$$

$$\text{Freundlich equation: } X=KC^{1/n} \tag{4}$$

$$\text{Temkin equation: } X=a+b\ln C \tag{5}$$

Where C is the equilibrium concentration in emulsion (g/*l*), X is the amount of oil adsorbed per unit mass of adsorbent (g oil/g). K, and (a, b) are constants of each adsorption model. X$_m$ is the max-

Table 1. Isotherm parameters for oil/water emulsion adsorption by untreated and treated OPEFB fibers

Isotherm			R^2
Langmuir	K	X_m	
Fresh fiber	−0.2998	−0.1239	0.9061
Silylated fiber	0.2630	0.7594	0.9629
Freundlich	K	1/n	
Fresh fiber	0.3195	1.3247	0.8965
Silylated fiber	0.4454	0.7934	0.9009
Temkin	a	b	
Fresh fiber	0.0904	0.2067	0.9307
Silylated fiber	0.1975	0.1454	0.8482

imum oil adsorption (g oil/g) used in the Langmuir model. 1/n represents the heterogeneity factor (1/n) for the Freundlich isotherm. To find all parameters for the adsorption isotherm equation, the linear least squares method was used.

Linearized Langmuir, Freundlich, and Temkin isotherms for the system of oil emulsified in water of untreated and silylated fiber (1%TMCS, 3 hr) were tested for the best fit. The isotherm parameters as determined by the intercepts and slopes of the linear regressions are reported in Table 1. A factor n (reciprocal of power facor, 1/n), represents adsorption possibility in the Freundlich isotherm. The results disclose that 1/n values for untreated and silylated fibers were 1.325 and 0.7934, respectively. This shows the treated fiber preferred oil sorption more than fresh fiber. Compared with R^2 values of untreated fiber for each adsorption model, it was found that Temkin (R^2=0.931) was best suited to describe the adsorption behavior.

Adsorption behavior could not be explained by the Langmuir isotherm for untreated fiber because of negative parameters, as presented in Table 1. As shown in Fig. 5, the untreated fiber isotherm corresponded to IUPAC type III. This adsorption indicated a cooperative adsorption related highly to the interference between adsorbed solute molecules with adsorbate. However, post-modified fibers showed its adsorption behavior close to Langmuir model with R^2=0.963. A dimensionless term of separation factor, R_L, could be expressed by the following equation [Hall et al., 1966]:

$$R_L = \frac{1}{(1+KC_o)} \tag{6}$$

Where C_o is the initial concentration used in each test run (g/*l*), and K is Langmuir constant. The resulting R_L values for every concentration plotted in Fig. 6 show that all data falls between 0 and 1 representing favorable adsorption of oil emulsified in water on silylated fibers. According to R_L values, treated fibers could represent a favorable adsorbent for low oil concentration. The maximum oil adsorption (g oil/g) at this low concentration was approximately 0.76 g oil/g fiber.

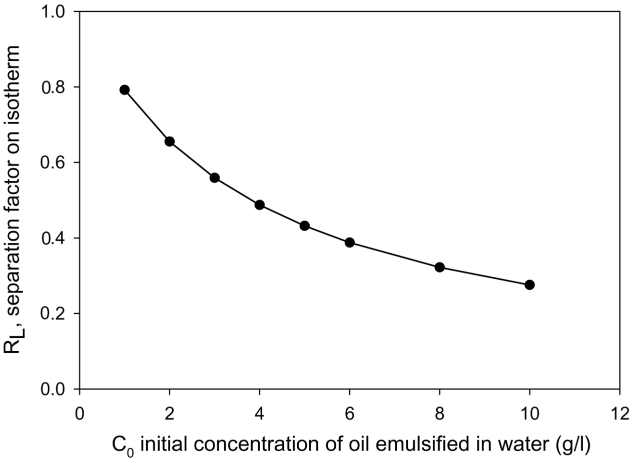

Fig. 6. Separation factors for Langmuir isotherm, R_L.

CONCLUSION

The oil palm empty fruit bunch fibers were modified by silylating agents to enhance absorbability of oil emulsified in water. SEM images show the open pores after washing out by mercerization and silylation. By FTIR, the fibers after silylation were removed hydroxyl group on fiber due to substitution reaction. The results showed that an optimal condition to reach the equilibrium silylation reaction was under a concentration of 1%wt and 3 hr aging time. Oil absorbability at low concentration emulsified in water on silylated fibers was greater than that on untreated fiber. The Langmuir isotherm showed the best fit with the experimental adsorption equilibrium data for silylated fiber.

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