VNU Journal of Science: Natural Sciences and Technology, Vol. 32, No. 4 (2016) 205-211

Modified Tung Oil and Its Application in Oil-Contaminated Water Treatment

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Received 01 August 2016
Revised 30 August 2016; Accepted 01 September 2016

Abstract: The wastewater issued from industrial firms, particularly in the fields of electronics and mechanics is often contaminated with oil/grease (used in maintenance of components, equipment and materials,...) and the oil amounts is also exceeding the permitted threshold for industrial wastewater. The treatment of such wastewater is often complex with several steps and needs specialized polymers that are imported, normally derived from petroleum and expensive. In this study, we propose to synthesize oil-water separating agents from natural plants (tung oil) that are abundant in Vietnam and environmentally friendly. The use of these products with a simple separation process enables the effective separation of the contaminating oil in water.

Keywords: maleated tung oil, maleic anhydride, oil-water separating agent, environmental treatment

1. Introduction

Vietnamese industry has witnessed an increasing development with the rapid rise of industrial firms, particularly in the fields of electronics, mechanical. Wastewater issued from these units is often contaminated with oil contents (genarated from cleaning processes of oily electronic components, machinery repair and maintenance...) exceeding the threshold allowed for industrial wastewater [1]. In addition to the negative impact on the surface water quality, oily wastewater is likely to infiltrate into the soil or be entrained with rainwater into the aquifers and thereby potentially affect the quality of groundwater [2, 3].

The treatment of oily wastewater is complicated because oil can be in multiple states in water, especially when oil is dispersed in water to form stable emulsion systems. To deal with this kind of oily water, it has often to use specialized demulsifiers (or emulsion breakers) based on high cost polyelectrolytes (usually synthetic polymers containing charged groups) derived from petroleum [4].

Vietnam has a rich flora with abundant resources of vegetable oil wherein tung oil has been studied and applied in various fields such as paint and coating (alkyd paint and oil paint), furniture, leather, printing industries, etc... [5]. Tung oil (TO) has many applications thanks to

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certain important characteristics that some other vegetable oils do not possess such as high thermal resistance, water resistance and salt tolerance. Tung oil contains fatty acids, principally α–eleostearic acid (about 80%) having conjugated double bonds that are easily modified to create new materials with different characteristics [6].

In this paper, we focused on tung oil modification by maleation using maleic anhydride (MA) in order to create materials which can be used as effective agent for the separation of oil-water emulsion system.

2. Materials and methods

2.1. Materials

The chemicals (KOH 85%, NaOH 99%, HCl 37%, Maleic anhydride 99%) were purchased from Merk. Nghe An tung oil was F type (Aleurites Montana) that has a yellow color and a density of 0.933-0.945 $g.cm^3$ at 25 °C. Castrol motorcycle lubricant was used in oil-water separating tests.

2.2. Characterization of tung oil

Determination of acid value. The acid value of vegetable oils is defined as the number of mg KOH needed to neutralize free acid contained in one gram of oil. It is determined according to TCVN 2639 -1993.

About 5 g of the oil sample was weighed (accuracy of 0.001g) and taken into a 250 mL conical flask containing 50 mL of solvent mixture (diethyl ether/ethanol with volume ratio 2:1). It was then titrated against 0.1053 N KOH in ethanol using phenolphthalein (5 drops) as indicator until a slight pink colour was appeared. For this titre value, the acid value (I_a) was calculated by formula:

$$I_a = \frac{56.11 \times 0.1 \times V}{m}$$

Where m is the weight of the oil sample taken in g; V is the volume of KOH in mL.

Determination of saponification value. The saponification value is defined as the number of mg KOH required to completely saponify 1 g of oil. Saponification value is determined according to TCVN 2633-1993.

About 2 g of oil sample was weighed (accuracy of 0.001g) and transferred into a 250 mL conical flask. 25 mL of 0.5 N alcoholic KOH was added and heated to reflux (shaken well from time to time) for about two hours (till the reaction was complete and the liquid becomes clear). Subsequently, to this solution, 0.5 mL of phenolphthalein was added and the mixture was titrated against a standard solution of 0.4901 N HCl until the pink colour disappeared. A blank experiment was simultaneously conducted in the same way without oil (containing only 25 mL of 0.5 N alcoholic KOH). Saponification value (X) of oil was calculated using the following formula:

$$X = \frac{(V_0 - V_1) \times 28.055}{m}$$

Where V_o is the volume of HCl consumed for blank (V_o = 24.50 mL); V_1 is the volume of HCl consumed for oily sample (mL); m is the mass of the oily sample (g); 28.055 is the number of mg of KOH used for 1 mL of 0.5 N HCl.

2.3. Modification procedure of tung oil

TO and MA were weighed and taken into a one neck-round bottom-flask fitted with a reflux condenser. The flask was heated at temperature of 170 ± 2 ºC using a silicone oil bath for 1 hour. When the reaction finished, the product was obtained as a viscous yellow liquid. The reactant composition for tung oil maleation is presented in Table 1.

Table 1. Reactant composition for the maleation reaction ($\overline{M}_{TO} = 871.9$ g.mol^{-1})

Samples	TO (g)	MA (g)	TO/MA molar ratio	
			initial	after reaction
TOMA 1	90.2	1.0	1: 0.1	1: 0.1
TOMA 2	90.0	2.0	1: 0.2	1: 0.2
TOMA 3	90.7	5.1	1: 0.5	1: 0.5
TOMA 4	90.2	10.1	1: 1.0	1: 1.0
TOMA 5	90.0	15.2	1: 1.5	1: 1.5
TOMA 6	90.3	20.3	1: 2.0	1: 2.0

2.4. Treatment of oily wastewater

Preparation of oily wastewater samples. 150 mL of waste oil (motorcycle oil) was added into 100 mL of industrial detergent. The mixture was well stirred for 15 minutes and then diluted to obtain 5 liters of oily wastewater sample. The obtained samples were emulsion systems that remained stable for 2 months without phase separation. The oil content in this emulsion is 24000 mg.mL^{-1}.

Oil-water separating procedure. 400 mL of oily wastewater was added into a 1 L beaker. 0.1 mL of maleated tung oil was added with stirring for about 5 minutes. A neutralizing solution (an acid solution) was added gradually with controlling the pH value and the turbidity of aqueous phase until a maximum transparency. The solution was allowed to rest for 5 minutes for complete phase separation. Finally, a suction device was used to take the oil layer (upper) out of the aqueous layer.

2.5. Characterizations

Proton nuclear magnetic resonance spectroscope (^{1}H NMR) was analyzed on a Bruker Avance 400 MHz in $CDCl_3$ solvent at room temperature at the Faculty of Chemistry, VNU University of Science, Hanoi.

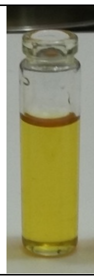
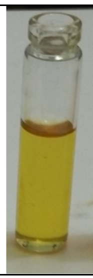
The turbidity was measured using a HACH 2100Q Portable Turbidimeter at the Faculty of Chemistry, VNU University of Science, Hanoi.

The determination of oil content in oily wastewater was conducted according to TCVN 4582 at Testing Laboratory of chemicals and material (TCM), R&D Center of additives and petroleum products - VILAS 067.

3. Results and discussions

The liquid products obtained from the maleation with different TO/MA ratios were entirely homogeneous and transparent (no observation of MA crystals) at the reaction temperature (170 °C) or at room temperature (Table 2). This phenomenon suggests that the reaction between maleic anhydride and tung oil has been complete (any amount of unreacted MA in the reaction mixture will lead to a crystallization while cooling to room temperature).

Table 2. Products obtained from maleation of TO at 170 °C at different TO/MA molar ratio

TO/MA molar ratio	1:0	1:0.1	1:0.2	1:0.5	1:1.0	1:1.5	1:2.0
Image of TOMA							

The [1]H NMR spectra of TO and maleated TO are presented in Figure 1. When comparing the [1]H NMR spectrum of maleated TO (Figure 1b) to the one of initial TO (Figure 1a), we didn't observe any peak at 7.04 ppm attributed to free maleic anhydride, which means MA has reacted off. Figure 1b revealed the formation of new peaks at 3.2-3.5 ppm and 5.85 ppm corresponding to the protons **H12** and protons **H7'** respectively. This allows clarifying the bonding of MA to the conjugated double bonds on the hydrocarbon chain of TO (scheme 1).

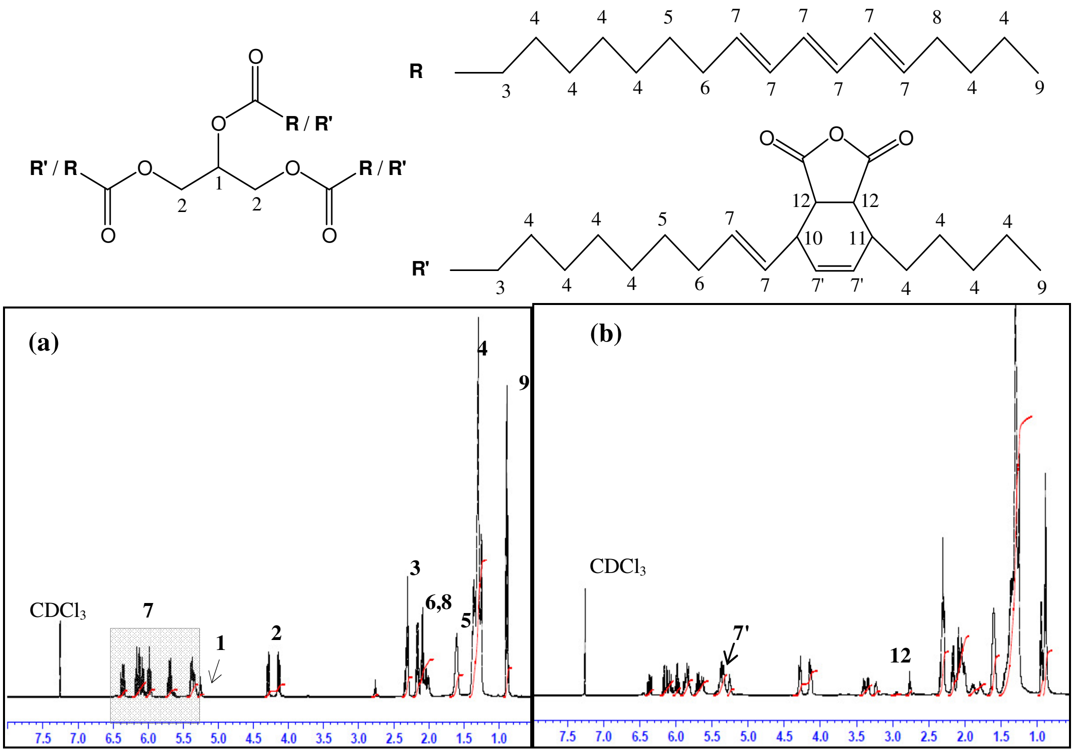
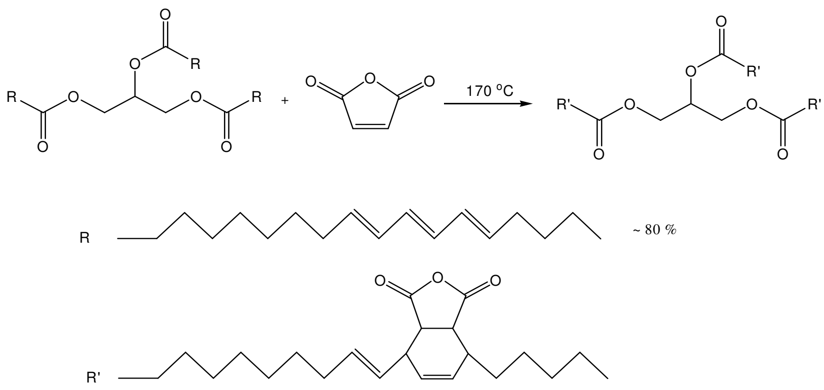


Figure 1. [1]H NMR spectra of TO (a) and maleated TO (b).



Scheme1. Grafting reaction of MA on TO.

The acid value, saponification value and ester value of tung oil were determined and presented in Table 3. From the obtained ester value, we can estimate the approximate average molecular weight of the triglyceride in tung oil:

$$\overline{M} = \frac{3 \times 56.11 \times 1000}{E} = 871.9 (g.md^{-1})$$

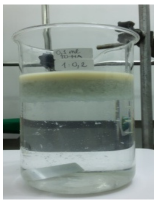
Subsequently, the acid value was also determined for maleated TO samples obtained with different TO/MA molar ratios. The results presented in tabe 2 showed that the acid value of maleated TO increased with MA content, that can be explained by the hydrolyse of anhydride functions during the titration to form acid groups [4].

Table 3. Saponification value, acid value, ester value of tung oil and maleated tung oils

Samples		Acid value, I_a (*mg* KOH/1 *g* oil)	Saponification value, X (*mg* KOH/1 *g* oil)	Ester value, E = X - I_a (*mg* KOH/1 *g* oil)
Tung oil	TO	18.6	211.7	193.1
Maleated tung oil	TOMA 1	26.7		
	TOMA 2	34. 5		
	TOMA 3	46.4		
	TOMA 4	87.8		
	TOMA 5	115.5		
	TOMA 6	138.9		

The study of TO/MA molar ratio effect on the separation efficiency is shown in Table 4. It can be seen from the turbidity values of different samples that two TO/MA molar ratios of **1:0.2** and **1:0.5** gave the best results corresponding to the best separation efficiency. TOMA with higher MA proportion will require higher amounts of chemicals for the same separation efficiency. Thus, in practice, the use of maleated TO with low MA proportion will be beneficial in economic terms due to using less chemicals.

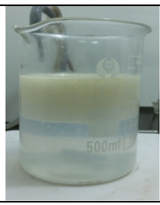
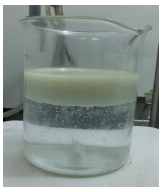
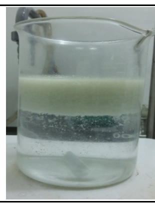
Table 4. Results of oily wastewater treatment with TO or TOMA

Samples	Emulsion before treatment	After treatment with					
		TOMA 1	TOMA 2	TOMA 3	TOMA 4	TOMA 5	TOMA 6
Turbidity (NTU)	1950*	0.29	0.19	0.16	0.21	0.22	0.20
Images		 treated with TOMA 2					

*A dilution of 10 times was required (the limit of the turbidimeter is 1000 NTU) that brought to a turbidity of 195 NTU.

To study the pH effect during the separation process, the TOMA 2 sample with TO/MA molar ratios of 1:0.2 was used. The turbidity was measured in function of pH values and presented in Table 5. It is shown that the solution began to separate into two phases with an pH decrease to about 5.4 and the phase separation was more thoroughly (as the aqueous layer more transparent) when the pH values was in the range of 4.0 - 4.5. At lower pH values, the solution became turbid again. These results showed that the best pH value for oily wastewater treatment is 4.0 and the average turbidity of aqueous phase measured in this case is 0.18 NTU. After treatment, the wastewater has an oil content of 8.9 $mg.mL^{-1}$ lower than the value permitted for industrial wastewater (10 $mg.mL^{-1}$) according to QCVN 40:2011/BTNMT standards [1].

Table 5. pH influence on the oil-water separation process using TOMA 2 as separating agent.

pH	13.5	11.5	5.4	4.5	4.0	3.0
Turbidity (NTU)	1950	1050	150	2.6	0.18	580
After treatment						

The mechanism of oil/water separation is described as follow. Once the maleated tung oil was added into the oily wastewater with stirring, the anhydride group that was grafted on oil molecules would be hydrolyzed, which generated molecules containing hydrophilic carboxylate group ($-COO^-$). The products of hydrolysis reaction at this time acted as a surfactant (emulsifier) because they have oil-loving tails linking to oil-droplets, which causes an aggregation of oil-in-water emulsion droplets to form larger droplets. The later still remained dispersed in water due to hydrophilic carboxylate groups located at the surface of oil droplets and oriented outward. Subsequently, when neutralizing the oily water by an acid, carboxylate anions transformed into carboxylic groups (-COOH), which reduced the dispersibility of emulsion droplets in water. Droplets with similar nature would aggregate to form larger particles and finally cause a phase separation wherein oil-layer will float or sediment depending on the density of oil-droplets compared to water.

4. Conclusion

The oil-water separating agents based on tung oil have been succesfully synthesized by a maleation conducted at temperature 170°C with various TO/MA molar ratios from 1: 0.1 to 1:2.0. The factors affecting the oil-water separation process have been investigated such as TO/MA molar ratio and pH, thereby the optimum conditions for the oil-water separation were determined as follows: TO/MA molar ratio = 1:0.2; pH range of 4.0 - 5.0 (the best pH value is 4.0. The water after treatment has an oil content allowed for the industrial wastewater.

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Dầu trẩu biến tính và ứng dụng trong xử lý nước nhiễm dầu

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Tóm tắt: Nước thải của các cơ sở công nghiệp, đặc biệt trong lĩnh vực điện tử, cơ khí thường bị nhiễm một lượng dầu (sử dụng trong bảo quản linh kiện, thiết bị, vật liệu,...) vượt quá ngưỡng cho phép đối với nước thải công nghiệp. Việc xử lí nước thải này thường phức tạp, trải qua nhiều giai đoạn và thường sử dụng các polyme chuyên dụng, nhập ngoại và có nguồn gốc từ dầu mỏ với giá thành cao. Trong nghiên cứu này chúng tôi đề xuất tổng hợp hóa chất phân tách dầu - nước từ nguồn nguyên liệu tự nhiên (dầu trẩu) rất phong phú tại Việt Nam và thân thiện với môi trường. Việc sử dụng hóa chất này cho phép tách loại dầu nhiễm trong nước một cách dễ dàng, hiệu quả với quy trình đơn giản.

Từ khoá: Dầu trẩu biến tính, anhidrit maleic, tác nhân tách dầu-nước, xử lý môi trường.