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CHEMICAL MODIFICATION OF CAT EYE DAMMAR WITH PHOSPHORIC ACID: EFFECT ON DENSITY AND EFFECTIVENESS AS EMULSION STABILIZER

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ABSTRACT

Cat eye dammar has been known as emulsion stabilizer but it is less effective than some other ones, such as brominated vegetable oil and sucrose acetate isobutyrate. Modification using phosphoric acid 85% (w/w) for one hour at 60 °C could increase the density of dammar from 1.04-1.06 g/mL to 1.17 g/mL. Emulsion made of modified dammar was more stable than that of raw dammar or SAIB but less stable than that of BVO. Modified dammar seemed to be 10-20% more efficient in preparation of emulsion compared to SAIB and raw dammar. Acute toxicity test indicated that modified dammar is practically non-toxic.

Keywords: *chemical modification, dammar, density, emulsion, non-toxic, stabilizer*

INTRODUCTION

Emulsion is unstable system because it is consisted of two immiscible liquids, such as oil and water. Emulsion destabilization could be impeded by some strategies, such as adjusting the droplet size and concentration, increasing the viscosity of continuous phase, and adjusting oil density to be nearly equal to water density. Adjusting droplet size could be conducted by appropriate instruments and processing. Increasing continuous phase viscosity could be done by adding thickener while increasing oil density could be done by adding weighting agent [1].

Chemical modification has been done to make emulsion stabilizers, especially weighting agents. Brominated vegetable oil (BVO), the most effective weighting agent, is made by brominating double bonds in vegetable oil so that the density of vegetable oil could increase from 0.9 to 1.3 g/mL. Sucrose acetate isobutyrate (SAIB) is another weighting agent, synthesized by substituting the hydroxyl of sucrose to acetyl and isobutyrate in order to change this hydrophilic and water soluble characteristic to become hydrophobic and oil soluble. BVO and SAIB are not safe for human [2-4].

Dammar resin is non-timber forest product from the stem of *Dipterocarpaceae* family, such as genera of *Shorea*, *Vatica,* and *Hopea.* The resin is obtained by taping the stem and let the resin come out and solidify for 2-4 weeks, so that it may contain some dirt. The bark also may contaminate the resin since the resin is very sticky and needs axe to be harvested. There are about 600 species of dammar and cat eye dammar from *Shorea javanica* is the best one [5]. Functionality of cat eye dammar as weighting agent has been known since tenth years ago, but it is the least effective since the density is the lowest compared to that of BVO or SAIB [6-8]. Therefore, it is very challenging to increase dammar density so that it can be used as effective weighting agent without altering its safety.

MATERIALS AND METHOD

Materials

Dammar resin from the stem of *Shorea javanica* was physically purified by The Research and Development Center for Forest Products, The Ministry of Forestry to remove dirt. This purified dammar was casted as blocks and milled to make it more miscible with phosphoric acid. Other materials such as phosphoric acid food grade (85% w/w), purified arabic gum (Caragum), BVO (density 1.33 g/mL, from Narda Tita), SAIB (density 1.12 g/mL, from United Chemicals), and coconut oil were used for preparation and analysis. Commercial feed, drinking water, corn oil, and female-and-healthy adult rat (*Sprague Dawley*) were used to conduct acute toxicity test of modified dammar.

Dammar Resin Modification

Dammar flour was mixed with concentrated phosphoric acid at low-and-constant speed and certain temperature. Optimation of the modification process included concentration levels of phosphoric acid (70 and 85% w/w), weight ratio of phosphoric acid to dammar (1:1, 1.5:1, and 2:1), processing time (0.5, 1, and 3 h), and temperatures (26, 60, and 80 °C). Products were separated from the residue and washed until free from phosphates. Finally, products were dried using vacuum oven and its density was determined.

Py-GC/MS Analysis

For py-GC/MS analysis, dammar was analyzed on py-GC/MS QP 2010 Shimadzu. The sample was pyrolized, fractionated in GC column

and detected by mass spectrometer DB5. Temperature of pyrolisis, GC oven, injector, interface, and ion source were 600, 50, 280, 280 and 200 °C, respectively. Injection mode was split and carrier was helium. Identification of the components was based on comparison of their mass spectra with those of internal libraries: NIST (National Institute of Standards and Technology) library, Wiley library, Pesticide library, FFNSC (Flavor and Fragrance Natural and Synthetic Compounds) library and Drug library. Percentage of each component was calculated based on its peak area and the density was predicted automatically using ACDLABS 12.0.

Emulsion preparation

Dispersed phase was made by dissolved the weighting agent in coconut oil. Continuous phase was made by dissolving potassium sorbate in aquadest, then arabic gum was added slowly. Continuous phase was agitated until homogen. Finally, the dispersed phase was slowly added to continuous phase using high speed homogenizer (17000 rpm, 10 min). The composition of final emulsion was 7% (w/w) dispersed phase, 18% (w/w) arabic gum, 0.3% (w/w) potassium sorbate, and the rest was aquadest. The dosage of weighting agent was adjusted so that the density of dispersed phase is similar to that of aquadest.

Emulsion stability determination

Emulsion stability was determined by accelerated method. Fresh emulsion was divided into three parts: the first was used as control, the second and the last were centrifuged for 10 min at 1400 and 2800 rpm, respectively. Cream turbidity from each of them was determined directly by diluting 1000 times of emulsion with aquadest. The less the change of turbidity against centrifugation, the more stable the emulsion is.

Acute toxicity test

Test was conducted using single dose (5000 mg/kg bw) and follow the method used at Indonesian Food and Drug Control Agency [9]. Corn oil was used as carrier. If there is no toxicity sign in the treated group, there is no further experiment needed [10].

RESULTS AND DISCUSSION

Dammar Modification

Phosphoric acid concentration, weight ratios of reactants, time and temperature of reaction influenced product quality. Phosphoric acid 70% (w/w) means that molecule amount ratio of phosphoric acid to water is 2:5, while the weight ratio of phosphoric acid to dammar is 21:20. Phosphoric acid 85% (w/w) means that molecule amount ratio of phosphoric acid to water is 1:1, while the weight ratio of phosphoric acid to dammar is 51:40. Using phosphoric acid 70% (w/w) increased the density of dammar from 1.0402±0.0011 to 1.0983±0.0063 g/mL, while using phosphoric acid 85% (w/w) increased dammar density to 1.1674±0.0011 g/mL. Optimum weight ratio of phosphoric acid to dammar had been investigated from 1:1, 1.5:1 and 2:1. The result showed that the higher the ratio was, the higher the product density was. However, increasing the ratio from 1.5:1 to 2:1 is not effective anymore (Table 1).

Beside concentration of reactants, time and temperature of reaction also contributed to the weighting agent density. While the reaction is run for 30 min, the density of product is similar to that of raw dammar. While the reaction is run for 1 hour, the density of product increases as much as 12%, but when reaction is prolonged 30 minutes later, the density of product did not increased significantly anymore. Therefore, optimum time for dammar modification is 1 hour based on the quality (Table 2).

Optimum temperature for dammar modification is 60 °C. Non-spontaneous chemical reaction need activation energy which can be provided through heating. In this investigation, at temperature lower than 60 °C, reaction rate constant may be too low so that the reaction of dammar and phosphoric acid can't occur and dammar density could not be increased. On the other hand, at temperature higher than 60 °C, the dammar will aggregate immediately so the dammar inside could not react with phosphate further. Therefore, the selection process condition is summarized in Table 3. The yield of product is 97.70±1.30% (w/w) with a density of 1.1674±0.0011 g/mL. Comparing to other commercial weighting agent, the density of modified dammar is higher than that of wood rosin (1.06 g/mL), ester gum (1.08-1.10 g/mL), and SAIB (1.12-1.15 g/mL), but less than that of BVO which is not allowed to be applied as food additive [11].

Table 1. The Effect of Weight Ratio of Phosphoric Acid to Dammar on The Weighting Agent Density

Weight Ratio of Phosphoric Acid to Dammar	Density (g/mL)
1:1	1.1079±0.0019
1.5:1	1.1674±0.0011
2:1	1.1817±0.0017

Table 2. The Effect of Processing Time to Weighting Agent Density

Processing Time (hour)	Density (g/mL)
0.5	1.0359±0.0008
1.0	1.1674±0.0011
3.0	1.1727±0.0013

Table 3. Selected condition for dammar modification

Phosphoric acid conc, % (w/w)	:	85
Weight ratio of phosphoric acid to dammar	:	1.5:1
Temperature, °C	:	60
Processing time, hour	:	1

Analysis using Py-GC/MS showed that there were eight organophosphor compounds in modified dammar, some of them was predicted to have density higher than dammar (Table 4). It seems that the density of phosphorothioic acid, O,O-dimethyl O-(3-methyl-4-nitrophenyl)ester is the highest one.

Impact of weighting agent on emulsion stability

Emulsions were made using BVO, SAIB, raw dammar and modified dammar. Basic principle in evaluating the impact of weighting agent on emulsion stability followed the previous report [7]. All emulsions have the same total oil phase, aqueous and emulsifier percentages, the difference among emulsions is only on the type and dosage of weighting agent. Based on the effective dosage of weighting agent to increase coconut oil density nearly equal to water density, the dosage of modified dammar is about 10 and 20% less than that of SAIB and dammar gum.

Emulsion Stability Determination

Figure 1 showed that the turbidity of diluted BVO emulsion is the most stable among other ones. BVO is freely soluble in coconut oil, so the dosage of BVO is sufficient to minimize density difference between oil and water phase. Therefore, BVO emulsion is stable against creaming. Figure 1 also showed that the turbidities of diluted dammar emulsion after being centrifuged for 10 min at 1400 rpm and 2800 rpm are similar. It indicated that this emulsion has been fully destabilized after being centrifuged for 10 min at 1400 rpm and this is the least stable emulsion. Though the emulsion stability could not be determined as precise as it had been investigated in previous researchers [7], it is clear that the emulsion containing modified dammar is more stable than that containing raw dammar.

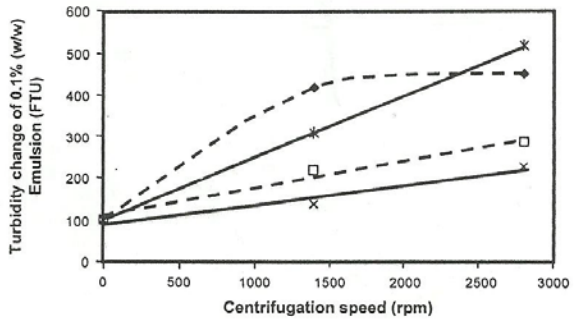
Acute toxicity of modified dammar

Modified dammar was suspended in corn oil at concentration 22.5% (w/w) so that it is easy for oral administration using syringe. Sample test for control group is 23.1 mL corn oil/kg bw and for treated group is 23.1 mL modified dammar suspension or equal to 5000 mg modified dammar/ kg bw. Modified dammar consumption did not yield any toxicity signs (Table 5). One day after being administered, all rats from control and treated groups suffered from diarrhea. This occurance was supposed to be because of high oil consumption. From the second day until the experiment finished, all rats had been normal anymore. There was also no significant difference of macro organs between control and treated groups after the experiment finished on the 14th day. Therefore, LD_{50} of modified dammar is higher than 5000 mg/kg bw, and this material could be categorized as practically non-toxic.

Tabel 4. Organophosphor compounds in modified dammar

Component	Molecular formula	Density (g/cm^3)	%
Phosphorochloridic acid, diethyl ester	$C_4H_{10}ClO_3P$	1.208 ± 0.06	0.36
Phosphorothioic acid, O,O-dimethyl O-(3-methyl-4-nitrophenyl)ester	$C_9H_{12}NO_5PS$	1.367 ± 0.06	0.32
Phosphoric triamide hexamethyl	$[(CH_3)_2N]_3PO$	1.032 ± 0.1	1.76
Tributylphosphine oxide	$(C_4H_9)_3PO$	0.87 ± 0.06	2.42
Triphenylphosphine oxide	$(C_6H_5)_3PO$	1.17 ± 0.1	0.55
Triethyl phosphine	$P(C_2H_5)_3$	*)	2.88
Triphenylphosphine	$P(C_6H_5)_3$	*)	0.94
Tri-n-butylphosphine	$P(C_4H_9)_3$	*)	0.66

*) Data is not available



--♦-- raw dammar, --□-- modified dammar, —Δ— SAIB, —x— BVO

Fig. 1. Change of diluted emulsion turbidity from several weighting agents

Table 5. Body Weight of Rats during Acute Toxicity Test (n = 5 for each group)

Day	Control (g)	Treated with 5 g/kg Modified Dammar (g)
0	196± 8.94	196±9.34
1	193± 6.58	203±6.96
5	198±10.37	203±8.20
8	217±11.41	217±5.86
12	218±14.12	222±6.87
14	227±15.65	226±6.54

CONCLUSIONS AND RECOMMENDATIONS

Modification of dammar using phosphoric acid increases dammar density from 1.0402±0.0011 to 1.1674±0.0011 g/mL and yields some organophosphor components. Further research on reaction mechanism and kinetics are necessary.

Modified dammar is practically non toxic. Further investigations for chronic toxicity and carcinogenity are still needed so that modified dammar could be approved by Codex as food additive.

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