Mechanism and kinetic model for glycerolysis of shellac

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Abstract. Shellac is a resin which is secreted from Kerria lacca, that can be utilized for coating and polyester. This material is brittle and stiff, hence modification of shellac is needed. One alternative to change its properties is by modification with glycerol. The purpose of this study is to investigate reaction between shellac and glycerol in the absence of catalyst. Moreover, in this research, the effect of hydroxyl position of glycerol is studied. In this present work, reaction was carried out for 2 hours and samples were taken every 15-30 minutes for analyzing the residual glycerol. Residual glycerol was analyzed using the periodic acid method. The reaction was carried out at various temperatures (160˚C, 170˚C, 180˚C and 200˚C). The results showed that glycerolysis reaction could be undertaken between 160˚C - 180˚C. In addition, the effect of ratio between glycerol and shellac was also investigated. In this study glycerol:shellac ratios were = 1:1; 1.5:1; and 2:1. The average relative error between experimental data and model in various temperature is 8.79%, while in the various ratio of glycerol and shellac is 8.26%. It showed that the kinetics model can describe well the reaction between glycerol and shellac.

1. Introduction

Products that have an environmentally friendly label are one of the competitiveness factors in selling goods in the international market. Moreover, environmentally-friendly products have convenience in export activities, because they are subject to cheap rates [1]. One product that is often used in everyday life is coating material.

It is often found that the coating material used is made of epoxy [2], polyurethane [3], acrylic [4], melamine [5], and others. These materials are made from petroleum, so the source is non-renewable. Moreover, the side effects of using these materials are harmful to the body and trigger various diseases [6-7]. Therefore, a coating material that is safe and renewable is alkyd resin. Alkyd resin is biologically degradable and easy to use [8].

Alkyd resin is the result of an esterification reaction between alcohol and carboxylic acid, wherein a polymer is formed. This happens because of the existence of functional groups in each reagent that interact and form a polymer chain [9]. One ingredient that has this functional groups is shellac.

Shellac is a resin, which was resulted from secretion of Kerria lacca. Shellac consists of carboxylate and hydroxyl group [10]. Structure of shellac consist of aliphatic hydroxyl and terpenic acid [11]. When hydrolyzed, shellac break down and form various kinds of constituents. These are aleuritic acid (35%), jalaric acid (25%), butollic acid (8%), and shellolic acid (8%) [10].

Shellac material has several weaknesses, which is stiff and brittle [12]. Therefore, modification of shellac is needed. In previous studies, film of shellac can be improvement its mechanical properties and percent elongation can be carried out with the addition of gelatin. Film of shellac had the percent...
ellac increased its tensile strength 5 times to break a complex chain of shellac. The addition of hydropropyl methyl cellulose (HPMC) to shellac increased its tensile strength. Respectively, when the percentage of shellac from HPMC-shellac mixture increased from 0.1% to 1% the tensile strength decreased almost 50% [14]. The addition of 2-amino-2-methyl-1-propanol (AMP) and ammonium hydroxide (AMN) can improve the puncture strength and percent elongation of shellac film. Film of shellac without and with AMP and AMN (60:40) can increase the puncture strength 3 times higher and percent elongation 2 times higher [15]. Other research, the addition of anhydrous succinate can reduce the brittleness of the shellac film. From this research showed that without and with succinic anhydrate (84.3 g) in shellac (115.7 g), the puncture strength improved from 0.32 MPa to 8.22 MPa. Meanwhile, the brittleness of film was reduced, which is indicated by the addition of succinic acid, the percent elongation increased 13 times higher [11]. This research was carried out by reacting shellac with glycerol (glycerolysis of shellac).

This present work investigated the reaction mechanism between shellac and glycerol. Proposed model is described in Equation (5) to Equation (9). In this study, experiment was conducted on various ratio of shellac:glycerol and glycerolysis temperatures.

Mechanism and model of reaction. Glycerolysis reaction is a chain breaking reaction using glycerol. This reaction is used to break a complex chain of shellac, so the simpler compound is formed, then restructured to form a compound that has a new character.

In this reaction there is an interaction between glycerol and shellac. Shellac has carboxylic group (-COOH) and glycerol has hydroxyl group (-OH). These groups are reacted to form new compounds (shellac-glycerol). This porposed model investigated the effect of the hydroxyl position on glycerol, these are primary hydroxyl and secondary hydroxyl. Each position of the hydroxyl group reacts with the carboxylic group in the shellac. Reaction glycerolysis of shellac, is shown in the Figure 1.

![Figure 1. Reaction scheme glycerol and shellac](image)

The model of the reaction mechanism between shellac and glycerol can be arranged as follows:

\[
R'_1 OH + R'' COOH \xrightleftharpoons{} R'' COOR'_1 + R'_2 COOH \quad (1)
\]

The chemical equation (1) and equation (2) can be simplified to be:
The rate of change in concentration of each component depend of time can be approximated by the
following equation:

\[
\frac{dC_{G_p}}{dt} = -k_1 C_{G_p}^\alpha C_B + k_{-1} C_C C_D
\]  

where \(C_{G_p}\) is primary hydroxyl concentration of glycerol (mg\text{eq}/g), \(C_{G_s}\) is secondary hydroxyl
concentration of glycerol (mg\text{eq}/g), \(C_B\) is concentration of shellac (mg\text{eq}/g), \(C_C\) is concentration of
shellac-glycerol (aliphatic) (mg\text{eq}/g), \(C_D\) is concentration of shellac-glycerol (cyclic) (mg\text{eq}/g), \(\alpha\) is
reaction order primary hydroxyl of glycerol, \(\beta\) is reaction order secondary hydroxyl of glycerol, and \(k_1, k_{-1}, k_2,\) and \(k_{-2}\) are rate reaction constant (g/(mg \text{eq}/minute)).

Equation (6) to Equation (10) were integrated simultaneously by guessing the values of \(k_1, k_{-1}, k_2,\) and \(k_{-2}\). The calculation of the reaction rate constant values will be obtained if the remaining glycerol
concentration of the model is close to the value of the remaining glycerol concentration of the data using
sum square of error (SSE) method. The obtained reaction rate constants will be analyzed to generate
activation energy values and frequency factors with the Arrhenius equation as presented in Equation
(10).

\[
k = A e^{\left(\frac{E}{RT}\right)}
\]

where \(k\) is reaction rate constant (g/(mg\text{eq}/minute), \(A\) is frequency factor, \(E\) is activation energy, and \(T\)
is temperature (K).

**Model I**

\[
\frac{dC_{G_p}}{dt} = -k_1 C_{G_p}^\alpha C_B + k_{-1} C_C C_D
\]

\[
\frac{dC_{G_s}}{dt} = -k_2 C_{G_s}^\beta C_B + k_{-2} C_C C_D
\]

\[
\frac{dC_C}{dt} = k_1 C_{G_p}^\alpha C_B - k_{-1} C_C C_D + k_2 C_{G_s}^\beta C_B - k_{-2} C_C C_D
\]

\[
\frac{dC_D}{dt} = k_1 C_{G_p}^\alpha C_B - k_{-1} C_C C_D + k_2 C_{G_s}^\beta C_B - k_{-2} C_C C_D
\]
\[ \frac{dC_B}{dt} = -k_1 C_G C_B + k_{-1} C_B C_D - k_2 C_G C_B + k_{-2} C_C C_D \]  \hspace{1cm} (15)

**Model II**

\[ \frac{dC_G}{dt} = -k_1 C_G^{0.5} C_B + k_{-1} C_C C_D \]  \hspace{1cm} (16)

\[ \frac{dC_C}{dt} = k_1 C_G^{0.5} C_B - k_{-1} C_C C_D + k_2 C_B C_B - k_{-2} C_C C_D \]  \hspace{1cm} (17)

\[ \frac{dC_D}{dt} = k_1 C_G^{0.5} C_B - k_{-1} C_C C_D + k_2 C_B C_B - k_{-2} C_C C_D \]  \hspace{1cm} (18)

\[ \frac{dC_B}{dt} = -k_1 C_G^{0.5} C_B + k_{-1} C_B C_D - k_2 C_G C_B + k_{-2} C_C C_D \]  \hspace{1cm} (19)

\[ \frac{dC_B}{dt} = -k_1 C_G^{0.5} C_B + k_{-1} C_B C_D - k_2 C_G C_B + k_{-2} C_C C_D \]  \hspace{1cm} (20)

2. Materials and Method

**Materials.** The materials used in this experiment are shellac provided by TB, Mas Erwin and glycerol (C\textsubscript{3}H\textsubscript{5}(OH))\textsubscript{3}) 53% purity provided by PT. Alkindo Mitratama. Meanwhile, analysis materials consist of ethanol (C\textsubscript{2}H\textsubscript{5}OH) 96% purity provided by CV. General Labora, periodic acid (HIO\textsubscript{4}) provided by Merck KgaA Company, natrium hydroxide (NaOH) pro-analytic provided by Merck KgaA Company, and distilled water provided by CV. General Labora.

**Methods.** The glycerolysis process is carried out on a three-necked flask assembled with a stirring motor, heating mantle, condenser, and thermometer. Shellac was cleaned first, then was mashed up. Glycerol and shellac were put in three-necked flask with a ratio of 1.5:1 (w/w). The reaction was carried out at 160°C with a stirring speed of 200 rpm for 2 hours. Every 15 minutes and 30 minutes, the sample was taken to analyze the remaining glycerol. This process was repeated for temperatures of 170°C, 180°C, and 200°C. The reaction was repeated with glycerol:shellac ratio at 1:1, 1.5:1, and 2:1 at 160°C.

Each sample that have been taken was placed in beaker and was added 25 mL of ethanol and 50 mL of periodic acid then left for one hour. The mixture was added of 50 mL of distilled water, then was titrated with 0.125 N NaOH solution. Blank titrations are also carried out with the same procedure without using samples.

\[ C_s = \frac{(V_f - V_0)}{m_{sample}} N_{NaOH} \]  \hspace{1cm} (21)

where \( C_s \) is concentration of glycerol (mg\textsubscript{eq}/g), \( V_f \) is NaOH solution to titrate blank solution (mL), \( V_0 \) is NaOH solution to titrate sample solution (mL), \( N_{NaOH} \) is normality of NaOH solution (mg\textsubscript{eq}/mL), and \( m_s \) is mass of sample (g).

3. Result and discussion

**Shellac identification.** Identification of shellac were characterized in order to determine whether the functional group were contained in this material. This present work aims to study the kinetics of the reaction between shellac and glycerol. The reaction in this study was glycerolysis, which was the chain breaking reaction using glycerol. This glycerolysis reaction is used to break up complex chains in the shellac, so that more simple compounds are formed, then restructured to form a compound that has better mechanical strength. Before carrying out the glycerolysis reaction, the hydroxyl numbers, acid numbers,
and ester numbers of original shellac were identified first. The results of the analysis show that original shellac has hydroxyl number 2.1528 mg eq/g, acid number 2.8000 mg eq/g, and ester number 3.6254 mg eq/g.

Effect of Reactant Ratio on Glycerolysis of Shellac. Analysis of residual glycerol was carried out at a temperature of 160˚C on various ratios between glycerol and shellac. Ratio of glycerol:shellac were 1:1; 1.5:1; and 2:1.

Model I
In this calculation, it was assumed that the glycerolysis reaction is an elementary reaction so that the order of reaction was 1 (glycerolysis reaction model I).

Experimental data concentration of glycerol were analyzed to find of $C_{Gp}$, $C_{Gs}$, $C_c$, $C_D$, and $C_B$ with Equation (11) to Equation (15). The average relative error between experimental data and model concentration of glycerol at ratio glycerol:shellac = 1:1; 1.5:1; and 2:1 were respectively 2.57%; 9.98%; and 14.60%. The values of reaction rate constants were obtained from each ratio of reactant and showed in Table 1.

Table 1. Reaction rate constants of glycerolysis of shellac in various ratios of reactant using model I.

| glycerol:shellac | $k_1$   | $k_{-1}$ | $k_2$   | $k_{-2}$ |
|------------------|---------|----------|---------|----------|
| 1:1              | 0.0032  | 0.0070   | 0.0030  | 0.0038   |
| 1.5:1            | 0.0039  | 0.0001   | 0.0039  | 0.0002   |
| 2:1              | 0.0050  | 0.0001   | 0.0052  | 1 x 10^{-5} |

From Table 1, the reaction rate constants change with the reactant ratio. The reaction rate constants should be relatively same, because theoretically what affects the change in the reaction rate constant is just temperature. Therefore, it is necessary to modify the model I.

Model II
The model I has not fulfilled the theory, so that modification is needed in model I. In this model the primary glycerol concentration has an order ($\alpha$) 0.5 and the secondary glycerol concentration has an order ($\beta$) 1. The following equation expressed the concentration of some components can be expressed in equation (16) until (20). The average relative error between experimental data and model concentration of glycerol at ratio glycerol:shellac = 1:1; 1.5:1; and 2:1 were respectively 2.43%; 9.39%; and 12.96%. The values of reaction rate constants model II were obtained from each ratio of reactant and showed in Table 2.

Table 2. Reaction rate constants of glycerolysis of shellac in various ratio of reactant using model II.

| glycerol:shellac | $k_1$   | $k_{-1}$ | $k_2$   |
|------------------|---------|----------|---------|
| 1:1              | 0.0060  | 0.0090   | 0.0009  |
| 1.5:1            | 0.0065  | 0.0002   | 0.0022  |
| 2:1              | 0.0064  | 0.0001   | 0.0031  |

Table 2 showed that the apparent reaction rate constants more same against the ratio of glycerol:shellac. To prove the apparent reaction rate constants whether affect with ratio of reactant or not, hence coefficient correlation analysis (R) was observed. Calculation of R can be expressed in Equation (22).

$$R_{x_1, x_2, ..., x_N, y} = \frac{\sum_{i=1}^{N} b_i \sum_{j=1}^{N} x_i y + b_{0} \sum_{j=1}^{N} x_j y + ... + b_{N} \sum_{j=1}^{N} x_N y}{\sum_{j=1}^{N} y^2}$$  \hspace{1cm} (22)
\[ \begin{align*}
\sum y^2 &= \frac{(\sum Y)^2}{n} + \sum x_i y_i - \frac{(\sum X)(\sum Y)}{n} \tag{23} \\
\sum x_i y_i &= \frac{\sum Y - \sum X Y}{n} \tag{24}
\end{align*} \]

where \( n \) is number of data, \( y \) is ratio of glycerol, \( x \) is apparent reaction rate constants, and \( b_1, b_2, \ldots, b_i \) are regression coefficient each variable. Coefficient correlation analysis showed that the R-value of model I was 0.1546, while model II was 0.0623. According Guildford empirical rule, if the R-value was in the range 0.00 - <0.20, hence the correlation between independent and dependent variable was very weak or can be ignored. Aftermath, the correlation between ratio of glycerol:shellac with apparent constant rate can be ignored in both model. But, model II was chosen because it had lower average error relative and R than model I. Both model can be presented with the graph shown in Figure 2.

**Figure 2.** Comparison of time course glycerol concentration between experimental data of varying ratio of glycerol:shellac and results obtained from (a) model I and (b) model II.

**Effect of Reaction Temperature on Glycerolysis of Shellac.** The temperature of glycerolysis was varied at 160˚C, 170˚C, 180˚C, and 200˚C in the ratio glycerol:shellac = 1.5:1. Experimental data of glycerol based on [16]. This calculation was approached with model II and the graph was shown in Figure 3.

Figure 3 showed that glycerol concentration decreased over time, because was consumed due to reaction. In the minute 0 until 60, the glycerol concentration decrease steeply. It indicated that glycerol and shellac concentration still high, hence the collision each molecule can happen easily. Therefore, the rate reaction became higher and the decreasing glycerol concentration became drastic. While, glycerol concentration in the minute 60 until 120 not significantly decrease, because glycerol and shellac concentration was decreased.

Glycerolysis of shellac could be observed at the range 160-180˚C, because at 200˚C shellac would be scorched. Therefore, the maximum temperature of glycerolysis of shellac was 200˚C. Respectively, the average error relative between experimental data and model at temperature 160˚C, 170˚C, and 180˚C are 9.39%, 8.96%, and 8.01%. The result of calculation reaction rate constants using SSE method in various temperature were shown in Table 3.

Table 3 showed that forward reaction rate constants \((k_1 \text{ and } k_2)\) had bigger value than backward reaction rate constants \((k^{-1} \text{ and } k^{-2})\). Hence, the glycerolysis of shellac could be approached as irreversible reaction. According [17] showed that glycerolysis between corn oil and glycerol was irreversible reaction, which are forward reaction rate constants more dominant than backward reaction constants, so the backward rate constants could be ignored. Moreover, \(k_1 \text{ and } k_2\) increased during the
increasing of temperature. It caused the temperature of reaction could be increased of kinetic energy each molecule, hence the intermolecular collision more frequent, then reaction rate more rapid.

![Figure 3.](image_url) Comparison of time course glycerol between experimental results of varying temperature reaction and results obtained from model.

### Table 3. Reaction rate constants glycerolysis of shellac in various temperature operation.

| T, °C | k₁          | k₋₁        | k₂          | k₋₂          |
|-------|-------------|------------|-------------|--------------|
| 160   | 0.0065      | 0.0002     | 0.0022      | 0.0008       |
| 170   | 0.0066      | 0.0002     | 0.0026      | 0.0002       |
| 180   | 0.0068      | 1.14 x 10⁻⁶| 0.0024      | 1.25 x 10⁻⁶  |

Apparent reaction rate constants at different temperatures were observed by equation (10). The calculated apparent activation energy and the frequency factor of primary hydroxyl group of glycerol and shellac were (E₁) 3669.6 Joule/mole and (A₁) 0.018 (g/mgeq)⁰.⁵/minute. While the activation energy and frequency factor of secondary hydroxyl group of glycerol and shellac were (E₂) 7245.2 Joule/mole and (A₂) 0.017 (g/mgeq)/minute. E₁ was greater than E₂, it introduced that primary hydroxyl group of glycerol was easier to react than secondary hydroxyl group of glycerol. It is caused the secondary hydroxyl group of glycerol has bigger steric hindered than primary group of glycerol.

### 4. Conclusion

This study the kinetics of the glycerolysis of shellac was studied in the absence of catalyst. The reaction model satisfactorily fitted, because of relative error between experimental data and model less than 10%. Proposed model can be approached with irreversible reaction. Apparent constants of reaction was introduced. The activation energy and frequency factor of primary hydroxyl group of glycerol and shellac are 3669.6 Joule/mole and 0.018 (g/mgeq)⁰.⁵/minute. While the activation energy and frequency factor of secondary hydroxyl group of glycerol and shellac are 7245.2 Joule/mole and 0.017 (g/mgeq)/minute. The maximum reaction temperature of glycerolysis was 200°C because at this temperature shellac started to be scorched.
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