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Original Research Article

Synthesis of Polyesters from AB Tung Oil-based Polyol Monomers Through Step-growth Polymerization Reactions

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Abstract

In this study, polyesters synthesized from AB Tung oil-based polyols (TOBPs) monomers via step-growth polymerization reactions. TOBPs are polyols made from Tung oil through a series of hydroxylation and epoxidation procedures. They have hydroxyl (OH) and carboxylic (COOH) functional groups. The polymerization was performed in a three-necked round-bottomed flask (250 mL) equipped with a magnetic stirrer, thermometer, and condenser. It is placed in an oil bath to maintain the reaction temperature. The generated moisture was collected using a vacuum pump. In the meantime, oxygen is being expelled from the reactor by nitrogen. The temperature and stirring speed were kept constant for 6 hours throughout the operation. According to the experiment, 150°C was the ideal temperature for polyesterification. The reaction rate constant rose by 4.73 to 19.99% with the addition of the p-TSA catalyst. The [COOH] and [OH] models were nearly identical to the experimental results, demonstrating the viability of the proposed kinetic model. According to the calculation's findings, polymerization without a catalyst yielded activation energies (*Ea*) and collision factors (*A*) of 27.2215 kJ/mol and 16.2965 g.mmol^{-1}.min^{-1}, respectively. Then, polymerization with catalyst decreased *Ea* and *A* values, which were around 26.4681 kJ/mol and 14.6746 g.mmol^{-1}.min^{-1}.

Keywords: Kinetics; Polyester; Polymerization; Tung oil-based polyols; TOBPs

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1. Introduction

Vegetable oil-based polymers (VOBPs) are reasonably priced and have a great deal of potential to replace products made of petroleum-based polymers. This is brought about by VOBPs' benefits of being renewable and biodegradable [1–3]. Vegetable oils work well as precursors to create a variety of polymers, including polyester, polyurethane, polyolefin, and polyester. VOBPs have the ability to generate hydrophobic polymers, in contrast to proteins and carbohydrates. Additionally, the structure of monomers made by VOPB is the same as that of monomers made from petroleum. Bio-based polymers have a wide range of uses because of these benefits [4–6]. Fatty acids, the main constituents of vegetable oils, may be transformed into useful molecules through a number of changes. These reactions took place in the unsaturated fatty acid carboxyl group, or alkyl chain [7].

One form of polymer that can be created from vegetable oils is polyester. For medicinal applications, synthetic biomaterials, including poly(e-caprolactone) and poly(lactic acid), have

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been widely used. To attain these specific qualities, vegetable oil-based polyester is manufactured. Condensation polymerization reactions between rubber seed oil monoglycerides and phthalic anhydride can create polyester resins [8]. Polyester can also be produced from reactions between epoxidized vegetable oils with a wide range of carboxylic acid anhydrides and catalysts in the form of tertiary amines, imidazole, or aluminium acetyl acetonate. The properties of the resulting polymer largely depend on the characteristics of the raw materials used. The development of plasticizer types from renewable resources is very important because the material has the potential for sustainability, biocompatibility, and biodegradability. Bio-based plasticizers that have been developed and used in the plasticization process consist of cardanol-based plasticizers, oxidized sunflower seed oil, rice fatty acids [9], oxidized soybean oil, and oleic acid polyester. However, this type of plasticizer requires high production costs. Therefore, research and development of bio-based plasticizers are still being conducted [10].

Vegetable oil that has undergone epoxidation is not only a potential replacement for phthalate plasticizers derived from petroleum but also a viable precursor to bio-based polymers [11]. The epoxidation of the double bond between the oxidizing agent and the alkyl chain to form fatty-acid-based epoxides is one of the possible processes [12]. The family of polymers that can be successfully made from epoxidized vegetable oil includes polyurethane, polyester, and polyether [5,6]. Oleic acid that has undergone epoxidation has two reactive functional groups in one molecule: an oxirane, also known as an epoxide, and a carboxylic group. As a result, it can also be used as a useful AB-type monomer to create bio-based polyester [13]. As an alternate method to create polymers with high molecular weight, the use of AB monomers in step-growth polymerization reactions has been acknowledged [14]. Although it still has a sizable polydispersity index, polymers with intrinsic microporosity for membrane application have been successfully produced from AB-type monomers [15]. AB-type sulfone-based monomers' phenyl halide and phenoxide self-condensed to form poly(ether sulfone) with a molecular weight of more than 110000 [16]. However, because the presence of both functional groups in the reaction system might result in a number of undesirable side reactions or an early stage of the polymerization process, AB-type monomers are difficult to synthesis [17].

Many previous studies have reported on the manufacture of vegetable oil-based polymers. Meanwhile, the manufacture of polyester from the AB Tung oil-based polyol monomers has not been carried out. This study offers a new approach in polyester synthesis by utilizing monomers containing two functional groups, namely hydroxyl (OH) and carboxyl (COOH). The main novelty of this research lies in the selection of these monomers, which are rarely used in conventional polyester production, to produce polyester chains with more flexible properties and have wider application potential. In addition, the raw material used in this study is tamanu seed oil, which is a renewable and environmentally friendly source of raw materials. Tamanu seed oil, which is rich in fatty acids, is used as a source of natural monomers, replacing petrochemical-based raw materials that are generally used in polyester production. With the combination of the use of two functional group monomers and natural raw materials, this research leads to the development of more sustainable and environmentally friendly polyesters, and has the potential to have better characteristics, such as higher mechanical strength and better biodegradability. Therefore, this study aims to synthesize polyester from AB Tung oil-based polyol monomers through step-growth polymerization reactions. Then, to increase the yield of polyester produced, this research also evaluated the influence of temperature and the addition of para-toluene sulfonic acid (p-TSA) as catalysts in polyesterification. Moreover, this study also evaluated second-order reaction kinetics.

2. Materials and Methods

2.1 Materials

Merck provided 99% glacial acetic acid, 98 wt% sulfuric acid, sodium thiosulfate, Wijs solution, crystal violet, 47 wt% hydrobromic acid in acetic acid, 30% hydrogen peroxide, potassium hydrogen phthalate, and potassium iodide. Tung oil was acquired from farmers in Indonesia's Majalengka and Sulawesi. The following items were bought from CV. Zirconia Jaya in Yogyakarta, Indonesia: potassium hydroxide, glacial acetic acid (AR Grade), sulfuric acid (98 weight percent), methanol, and pyridine. From CV. Multikimia in Yogyakarta, Indonesia, acetic anhydride and potassium hydrogen phthalate were acquired.

2.2. Polyesterification process

Tung oil, sulfuric acid, and the necessary quantity of glacial acetic acid were added to the reactor to create epoxidized Tung oil (ETO). Glacial acetic acid and tung oil had a mole ratio of 2:1. A certain amount of aqueous hydrogen peroxide (H_2O_2) was added dropwise over the course of 30 minutes to the reactor when the desired temperature was reached. ETO was isolated from the contaminants after the reaction

had been running for 4 hours [18,19]. The ETO was then supplied to the reactor in the calculated amount. In Erlenmeyer, specific concentrations of sulfuric acid and methanol (3% of the total solution) were combined. Methanol and ETO have a molar ratio of 10:1. The reactor was filled with a methanol and sulfuric acid mixture. The isothermal methanolysis processes took place for 4 hours at a temperature of 60 °C and a stirring speed of 600 rpm [20,21]. Warm distilled water was used to clean the polyol monomers made from AB Tung oil in the separation funnel. The oxirane number and hydroxyl value of the produced samples were then calculated.

The polymerization assembly was charged with the AB Tung oil-based polyol monomers. A three-neck round-bottom flask (250 mL) with a magnetic stirrer, a thermometer, and a condenser was used for the polymerization process. It was put in the oil bath to keep the reaction temperature constant. To collect the moisture, a vacuum pump was used. In order to keep oxygen away from the reactor, nitrogen gas (N_2) is pumped there. As a result, the polymer does not burn easily. For six hours, the operating conditions are maintained at a constant temperature (based on the temperatures assessed) and stirring rate (600 rpm). Temperatures of 120, 135, 150, and 165 °C were evaluated. Following that, a 2% p-TSA catalyst was used in various amounts during polymerization. Samples are taken at specific intervals.

2.3 Analysis

Polyester products produced at certain intervals are then analyzed for their oxirane number, acid number and hydroxyl number. In addition, to ensure the formation of polymers, functional group analysis with Fourier Transform Infra-Red (FTIR) Spectroscopy and molecular weight analysis with the Gel Permeation Chromatography (GPC) method are carried out.

(a). Oxirane number: A total of 0.5 samples were inserted into a sealed 100 mL Erlenmeyer. Then, 10 mL of glacial acetic acid was added to the Erlenmeyer. After that, 3 drops of Penta violet indicator are added to the mixture and titrated with HBr 0.1 N solution until it becomes green. It is recommended that during titration a micro burette is used and the top of the burette is closed using aluminium foil:

$$Oxirane\ number = \frac{V \times N \times 1.6}{m} \quad (1)$$

with V is titration volume (mL), N is normality of HBr (N), and m is sample mass (g).

(b). Acid number ([COOH]): The acid number is a measure of the number of free fatty acids, calculated based on the molecular weight of fatty acids or a mixture of fatty acids. The acid number is expressed as the number of milligrams of KOH 0.1 N used to neutralize the free fatty acids found in 1-gram of oil or fat:

$$Acid\ number = \frac{V_{KOH} \times C_{KOH} \times MW_{KOH}}{m} \quad (2)$$

where, C stands for concentration and MW denotes molecular weight.

(c). Hydroxyl value ([OH]): A 2.8-3.2 g polyol sample was put into a test tube and then added with 1-1.2 g / 0.9-1.1 mL of pyridine solution in acetic anhydride. The solution uses a ratio of pyridine to acetic anhydride of 1:3. The test tube was tightly closed (sealed) and shaken until smooth. The mixture was heated for 2 hours in a vertical position in an oven at a temperature of 150 °C then cooled. The mixture obtained was poured into a 500 mL Erlenmeyer flask containing 50 mL of water. The tube and lid were rinsed with hot water and then with cold water to a volume of 200 mL. The mixture was boiled under reflux condenser, cooled and the reflux condenser was rinsed. The cooled mixture was titrated with 0.5 N NaOH solution and 10 drops of PP indicator. Standardization was carried out by performing a blank solution on a pyridine solution in acetic anhydride (the same procedure but without using polyol and heating). If the sample contains free fatty acids, correction must be made:

$$Hydroxyl\ value = \frac{(V_1 - V_2) \times N_2 \times 56.1}{W} + Acid\ number \quad (3)$$

with W is sample weight for acetylation (g), V_1 is volume of KOH for blank titration (mL), V_2 is volume of KOH for titration of acetylated sample (mL), and N_2 is normality of KOH solution.

2.4 Kinetics Model

The kinetics model used in calculation is second order:

$$\frac{-d[COOH]}{dt} = k'[COOH][OH] \quad (4)$$

It has applied to the reaction with catalyst.

$$\frac{-d[COOH]}{dt} = k'_{cat}[COOH][OH] \quad (5)$$

The values of k' and k_{cat}' can be determined by fitting the data obtained from the experiment, namely the concentration of carboxylic acid [COOH] and the concentration of hydroxy [OH] with minimal error:

$$Error = \sum \frac{\left|([COOH]_{org})_{calc} - ([COOH]_{org})_{data}\right|}{([COOH]_{org})_{data}} + \sum \frac{\left|([OH]_{org})_{calc} - ([OH]_{org})_{data}\right|}{([OH]_{org})_{data}} \quad (6)$$

3. Results and Discussion

In this work, polyesterification was defined as the condensation polymerization of COOH and OH groups in polyol compounds. In polyol compounds, the COOH group is a function group at one end. The OH group in the middle of the polyol molecule is predicted to connect to this function group. One challenge to getting polyester with a long chain is the presence of significant stearic barriers. By monitoring a drop in the concentration of reactants in the mixture, one can gauge the rate of the polyesterification reaction [22]. Polyesterification is essentially a reversible process. As a result, vacuuming is used to remove the byproduct in order to reduce the risk of backlash while also increasing conversion. The effect of temperature on polyol polyesterification without catalysts, polyol polyesterification with catalysts, and polymer/polyester characterization will all be addressed in this section. The reaction scheme to illustrate the polyesterification is shown in Figure 1.

3.1 Effect of Temperature on Polyesterification without Catalysts

Tung oil-based polyols are used in this polyesterification as the basic ingredient. Since no more acid molecules are added, the initial hydroxyl concentration ($[OH]_0$) is greater than the initial acid concentration ($[COOH]_0$). Data on hydroxy concentration ([OH]) relating to reaction time at various temperatures are shown in Figure 2. The concentration of hydroxyl ($[OH]_0$) varies significantly, as can be seen from this chart. This is due to the fact that reaching the correct operating temperature is a prerequisite for determining t = 0 during data retrieval. It takes a while for high polymerization/polyesterification temperatures (120 –165 °C) to get to that starting point. As a result, when t = 0, the conversion of each reaction's temperature is different.

In this modeling of the polyesterization reaction, the start reaction time (t=0) is estimated empirically because what is shown in the figure or graph is not exactly at t=0. As explained earlier, in the figure t=0 is taken based on the time when the desired polyesterization reaction temperature is reached. The relatively high temperature of

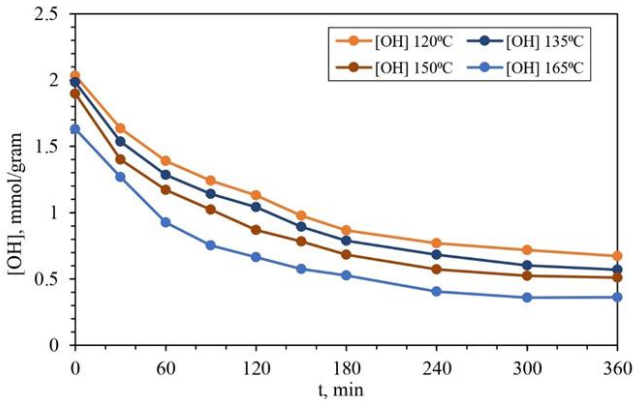

Figure 2. [OH] as a function of reaction time at various temperatures.

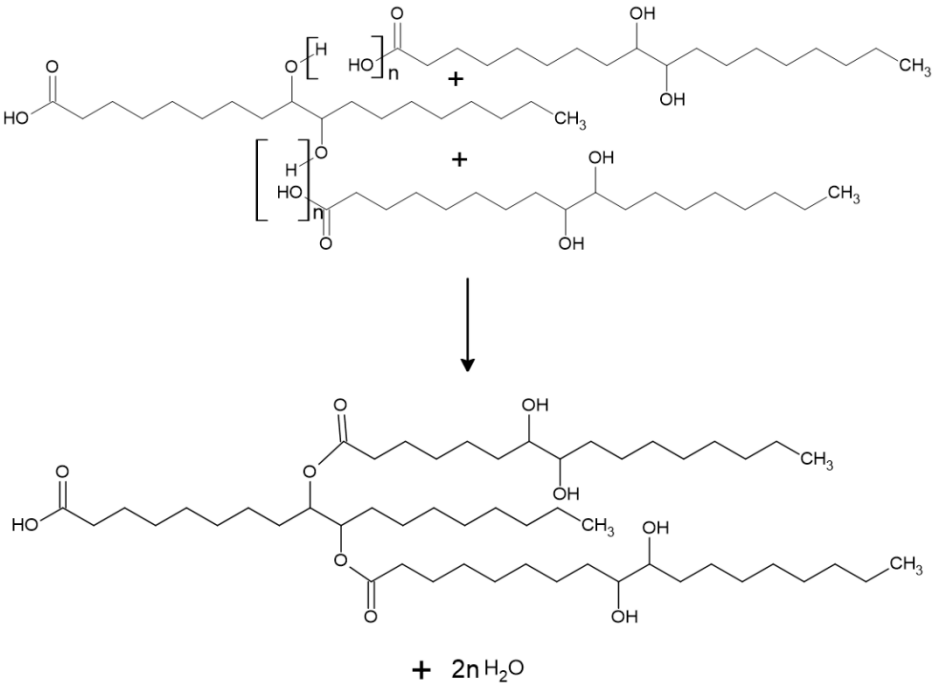

Figure 1. A reaction scheme to illustrate the polyesterification.

polyesterization (i.e. 120 – 165 °C) takes a relatively long time to reach that starting point. As a consequence at t = 0, each reaction temperature has a conversion ≠ 0 and varies. This empirical estimate is intended to estimate the actual time in the polyesterization process based on the trendline of experimental data.

In detail, the steps taken are: (1). Reset the raw data to change the initial concentration of [OH]0 and [COOH]0 becomes [OH] and [COOH] at the corresponding time to extrapolate the curve using the corresponding polynomial trendline. This data reset is performed at each temperature and [OH] and [COOH]; (2). Process new [OH] and [COOH] data simulations according to modeling submitted using Matlab. Results of [OH]m and [COOH]m obtained with minimum SSE; (3). Restore data to the original time.

The reaction temperature has a correlation inversely proportional to [OH], meaning that the higher the reaction temperature decreases [OH]. The increase in temperature increases the molecular kinetics of the particles present in the reactor, so that the collision between particles gets bigger and the reaction takes place faster. The increase in reaction time decreases [OH]. This is because as the reaction time increases, the contact and collision of reactant particles get larger, so more [OH] reacts. The rate of polyesterification decreases when functional groups are consumed. This means that the molecular weight of the polymer increases continuously, even at high conversion rates. The process is slow down as reactive groups decrease and it is no longer possible to react at a sufficient rate. In this process, the highest conversion was about 83.82% (against the OH cluster) and 94.95% (against the COOH cluster). This considerable conversion difference can be explained based on the composition of raw materials and the kinetics of chemical reactions. From the analysis of hydroxyl numbers and acidic numbers against polyols, it is known that $[OH]_0 > [COOH]_0$. In theory, because hydroxy groups and carboxylic groups have the same coefficient of reaction, the COOH group is a limiting reactant. As a result, COOH moles that react are the same as OH moles that react, and COOH conversion > OH conversion. In addition, the position of the COOH cluster at the end is relatively easier to react with compared to the OH cluster located in the center (there is large stearic resistance).

Figure 3 shows the concentration of carboxylic acid ([COOH]) as a function of reaction time and temperature. As with the [OH] discussion, temperature and time have a direct correlation to [COOH]. The higher the temperature, the greater the molecular movement of the OH group, so that the probability of collision with the COOH group is greater. The increase in temperature will increase the energy factor so that the collision factor increases [22]. From the figure, it appears that the decrease [COOH] can be categorized into three parts. Part 1 (at a reaction time of 0 to 90 minutes) processes very quickly; part 2 (at 90 to 180 minutes) processes at medium speed; and in part 3 (reaction time > 180 minutes), the decrease in [COOH] is slow. This is due to the initial mobility reaction or relatively high molecular motion of reactants. The existing monomers are spilling into each other quickly because the solution in the reactor is still not viscous. In Part 2, the mobility of reactant particles decreases as their viscosity begins to increase. In Part 3, the viscosity of the solution increases as more polymers are produced. In addition, the longer the reaction time, the closer the balanced condition is. As a result, the reaction went slow. This condition applies to all reaction temperatures evaluated.

The results of simulating the influence of temperature on polyesterification (without catalysts and without further acid) can be seen in Figure 4. From the figure, it appears that $[OH]_0 > [COOH]_0$. The decline in experimental data [OH] and [COOH] is relatively similar. This indicates that the mole [OH] that reacts is almost the same as the mole [COOH] that reacts. The evaluated kinetics model provides satisfactory results, where experimental data from [OH] and [COOH] fairly match the results of the model. Additionally, the deviation between the data and the model grows as the temperature rises (between 150 and 165 °C), especially for reaction times of more than 180 minutes. This problem arises because side reactions are more likely to happen at higher temperatures with longer reaction times. While there is no side reaction in the proposed kinetics modeling.

Table 1 displays the constant reaction rate for each temperature during catalyst-free polyesterification. The resulting constant has an order of 10^{-3} g.mmol^{-1}.min^{-1}. The constant value of

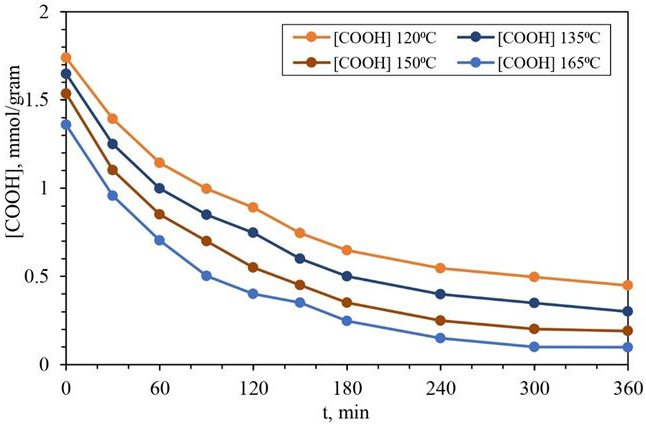

Figure 3. [COOH] as a function of reaction time at various temperatures.

the reaction rate in the temperature range of 120-165 °C is approximately 4.039×10^{-3} to 9.428×10^{-3} g.mmol^{-1}.min^{-1}. It is possible to determine the activation energy (*Ea*) and collision factor (*A*) by plotting the ln *k*' versus (1/*T*). Figure 5 shows correlation between *k*' and (1/*T*). The collision factor (*A*) value was 16.2965 g.mmol^{-1}.min^{-1}, and the activation energy (*Ea*) value was found to be 27.2215 kJ/mol. In the prior study, specifically polycondensation for the manufacture of poly(ethylene terephthalate), the *Ea* result in this reaction was different, which was about 11.76 kJ.mol^{-1} [23].

3.2 Effect of Temperature on Polyesterification with Catalyst

A catalyst is a substance that can accelerate the reaction without reacting (inert). In chemical kinetics, catalysts play an important role because they can lower activation energy but do not change reactant energy or the original product, so as not to change equilibrium. So, the reaction takes place faster. Figures 6 and 7 are curves that show a correlation between [OH] and [COOH] to the time and temperature of reactions in polyesterification with the addition of p-TSA catalysts. The p-TSA catalyst is solid with a melting point of about 103.2 °C. This polyesterification uses a 2% pTSA catalyst to speed up the reaction.

From Figure 6, it appears that all reaction temperatures used have a trend that is relatively constant over time. The longer the reaction time, the lower the concentration of hydroxy ([OH]). This decrease is caused by increased contact between reactant particles, resulting in increased collisions and greater reaction rates. However, the decrease [OH] within 240 minutes and above is insignificant. This condition is possible because the reaction is close to balanced. Temperature has an inversely proportional effect on [OH], where

Table 1. Polyesterification reaction rate constant without the addition of a catalyst.

T (°C)	*T* (K)	*k*' ×10^3 (g.mmol^{-1}.min^{-1})
120	393.15	4.039
135	408.15	5.163
150	423.15	7.064
165	438.15	9.428

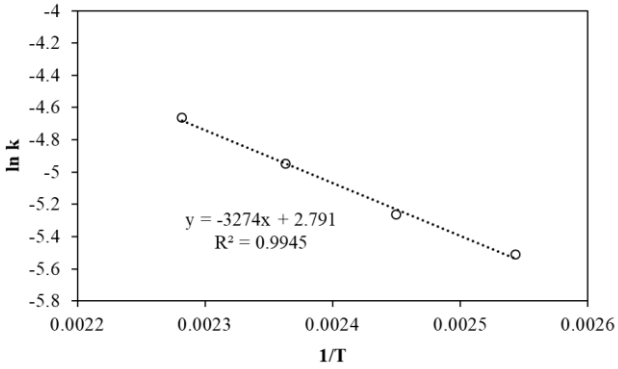

Figure 5. Correlation between *k*' and (1/*T*).

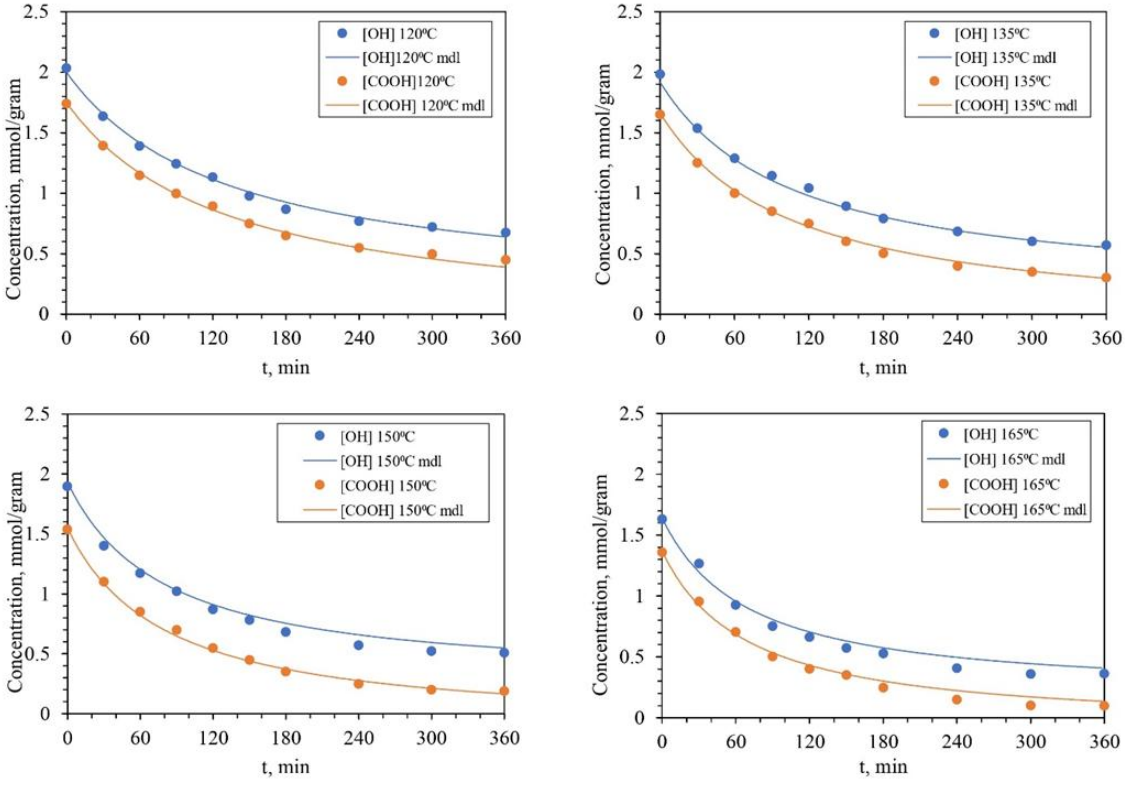

Figure 4. Results of modelling in the polymerization without catalyst.

[OH] as reactants decreases with the increased temperature. This happens because the kinetics and molecular motion of the reactant particles present in the reaction system increase with the increase in temperature. As a result, the effective collision between reactant particles increases, and the reaction rate becomes faster. The difference in temperature intervals of 15 °C provides different descriptions. At temperatures of 120 °C and 135 °C, there were significant differences [OH], especially at the beginning of the reaction. While at 150 °C and 165 °C, the difference [OH] is relatively small during the reaction (at the end of the reaction, the curve is almost tight). At the same time, the concentration of [OH] in polyesterification with this p-TSA catalyst is smaller compared to [OH] in polyesterification without catalysts. For example, at the end of the reaction, a polyesterification temperature of 120 °C was obtained at 0.6482 mmol/g (with catalyst) and 0.6729 mmol/g (without catalyst). This also applies to other temperatures and reaction times. Polyesterification at 150 °C and a time of 90 minutes resulted in 0.8123 mmol/g (with catalyst) and 1.0229 mmol/g (without catalyst). This is because catalysts accelerate the reaction rate by lowering activation energy, so [OH] as reactants will decrease faster in the presence of catalysts.

Figure 7 presents the [COOH] relating reaction time at different temperatures. Process variables, i.e., temperature and reaction time, have an inversely proportional correlation with [COOH]. This [COOH] decline is not much different from [OH]. Hydroxy groups (OH) and acid groups (COOH) are both reactants. As in the proposed model, acid groups and hydroxy groups have the same reaction coefficient (but the number of moles is initially different). Therefore, [OH] reacts almost the same as [COOH] reacts. The presence of p-TSA catalysts is proven to accelerate reactions. This can be seen from [COOH] at 135 °C and 120 minutes, obtained at about 0.6975 mmol/g (with catalyst) and 0.7474 mmol/g (without catalyst). With the catalyst, the number of reacted moles [COOH] increases, so the remaining [COOH] is smaller when compared to the reaction without the catalyst. The increase in reaction temperature from 120 °C to 150 °C has a significant effect. However, temperature changes from 150 °C to 165 °C showed no significant differences in [OH] or [COOH]. Therefore, from these data, it can be assumed that 150 °C is the optimum temperature for polyol polyesterification with a p-TSA catalyst.

In modeling this polyesterification reaction, the steps taken are the same as the previous one (polyesterification without catalyst). The [OH] and [COOH] data obtained from the experiment were processed first to reset the time. After that, the new [OH] and [COOH] data and k_{cat}' value guesses are included as inputs in the completion of the model. The principle of completion is the minimization of SSE. The results [OH] and [COOH] obtained, then returned to the original time. The concentrations [OH] and [COOH] of experiments and models are shown in Figure 8. The meaning "m" in Figure 8 is model. At all reaction temperatures, [OH] > [COOH] during the reaction. This is because the $[OH]_0$ contained in polyols is greater than the $[COOH]_0$. The reaction coefficients of the two groups are the same, meaning the number of moles of COOH reacting is about the same as the number of moles of OH reacting. Thus, it is logical that the measured concentration of hydroxy during the reaction is always greater than the carboxylic concentration.

The modeling results are quite satisfactory; the concentration of carboxylic and hydroxyl models is almost the same as the results of the experiment. Polyesterification with this catalyst has a different trend error than polyesterification without a catalyst. In non-catalytic reactions, the rise in temperature results in an even greater error, whereas in this reaction, the error is not directly proportional to the temperature. It is possible that the p-TSA catalyst not only serves to

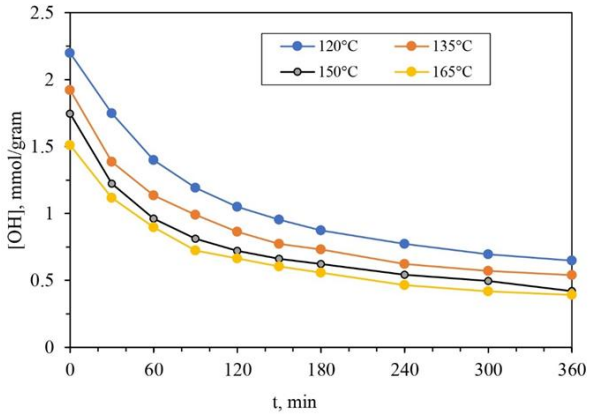

Figure 6. [OH] as a function of reaction time at various temperatures (polymerization with catalyst).

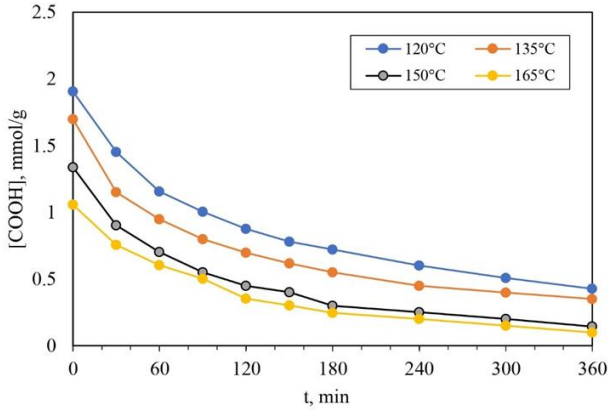

Figure 7. [COOH] as a function of reaction time at various temperatures (polymerization with catalyst).

accelerate the reaction but also directs the reaction. This catalyst function is also indicated by the results of [OH] and [COOH] produced in polyesterification with a catalyst being lower than the results of polyesterification without a catalyst. This applies to all temperatures and reaction times.

In the process of polyesterification with a catalyst, the highest conversion of about 84.18% (against the OH group) and 95.08% (against the COOH group). The conversion difference between the two groups is quite large because $[OH]_0 > [COOH]_0$, so the COOH cluster is a limiting reactant. In theory, because hydroxy groups and carboxylic groups have the same coefficient of reaction, COOH moles react the same as OH moles that react. As a consequence, COOH conversion > OH conversion. In addition, the position of the COOH cluster at the end is relatively easier to react to compared to the OH cluster located in the center (there is a large stearic resistance). So, it is possible that although the coefficient of reaction is the same, in real conditions, COOH moles that react are greater than OH.

The highest conversions (at t = 240 minutes and temperatures of 165 °C) obtained in polyesterification reactions with this catalyst were only slightly higher compared to conversions in reactions without catalysts. The addition of catalysts only gave conversion increases of about 0.13% (for hydroxy groups) and 0.43% (for carboxylic groups). However, at lower reaction temperatures, the difference is relatively significant. For example, at 120 °C, conversion is approximately 69.97% and 77.47% (without catalyst) and 72.03% and 79.21% (with catalyst). This is possible because, at high temperatures (i.e., 165 °C) and long reaction times, conversion is close to balanced conditions. That is, catalysts accelerate the achievement of balanced conditions.

The reaction rate constants obtained from the calculation of the kinetics model are shown in Table 2. The reaction rate constant increases with a rise in temperature. This corresponds to kinetics in general; the temperature increases the molecular motion of the reactant particles and enlarge their collision. As a result, the reaction rate is getting greater. This constant has a reaction order of 10^{-3} g.mmol^{-1}.min^{-1}, the same as in polyesterification without catalysts. However, the value is greater than the constant rate of the polyesterification reaction without a catalyst. At this polyesterification, the constant reaction rate ranges between 4.437×10^{-3} and 9.875×10^{-3} g.mmol^{-1}.min^{-1}. The p-TSA catalyst increases the reaction rate constant by approximately 9.85%; 12.61%; 19.99%; and 4.73% for temperatures 120, 135, 150, and 165 °C. This is in accordance with Arrhenius' law, which states that catalysts can decrease activation energy, thus magnifying the

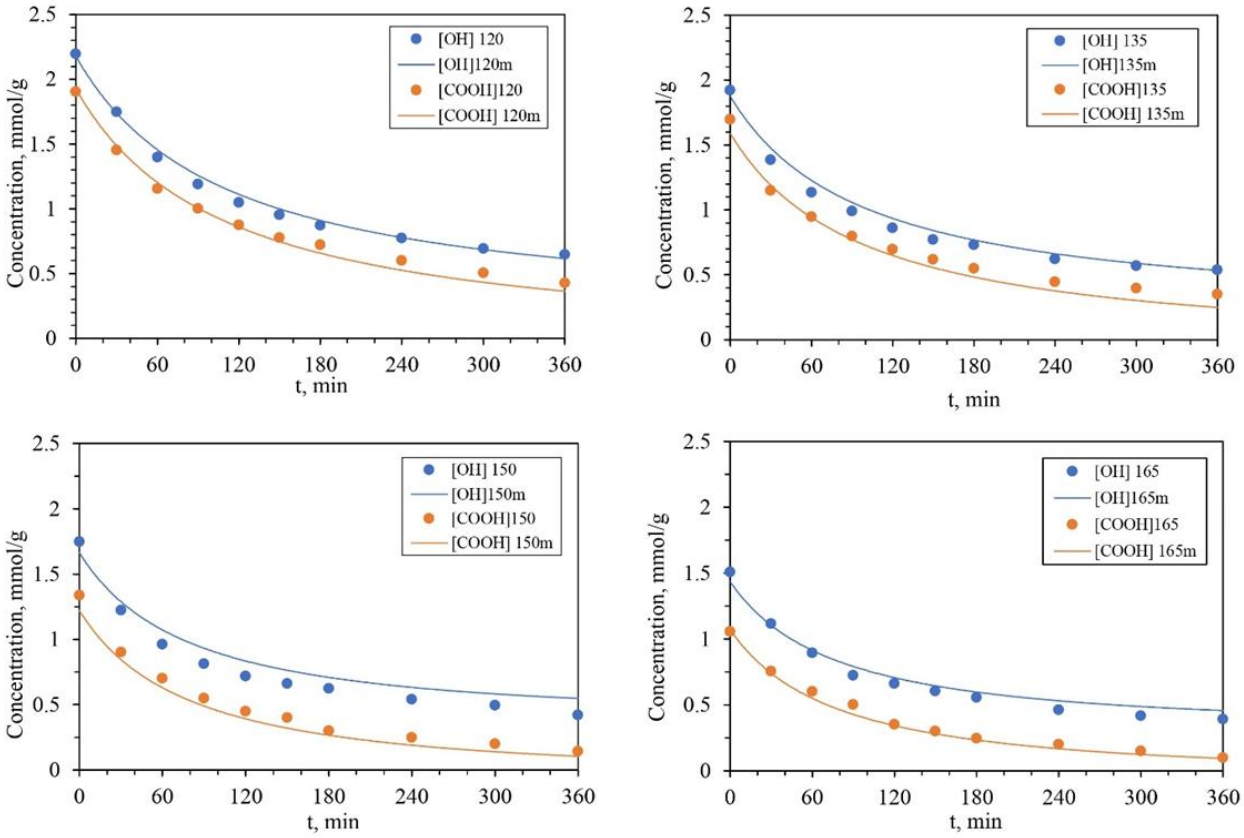

Figure 8. Results of modelling in the polymerization with catalyst.

constant reaction rate.

The activation energy parameters (*Ea*) and collision factor (*A*) can be determined from the Arrhenius equation. The modification of the equation obtains a correlation in k_{cat}' as a function of 1/*T*. The *Ea* value obtained is about 26.4681 kJ/mol and *A* is about 14.6746x10^{-3} g.mmol^{-1}.min^{-1}. The results of *A* and *Ea* in this reaction are in line with previous research, namely isoamyl alcohol hydrogenolysis [23]. When compared to the *Ea* value obtained in non-catalyst polyesterification (i.e., 27.2215 kJ/mol), catalysts can decrease activation energy by about 2.70%. This process demonstrates how catalysts play a role in accelerating reactions by reducing activation energy [23].

3.3 FTIR and GPC Analyses

FTIR analysis was performed on polyol and polymer samples produced at operating temperatures of 120 °C and 165 °C. The FTIR analysis results are shown in Figure 9. The Figure 9 (a) shows that the success of polymerization is clearly visible; where the peak of the -OH group (wavelength 3444.97 cm^{-1}) which is quite dominant in the polyol sample is almost invisible in the polymer sample. Likewise, the presence of the carboxylate group (-COOH) in the polyol is quite clear at a wavelength of 1636.74 cm^{-1}. This group is not visible in the FTIR results of the polymer. The -OH group reacts with the -COOH group to produce an ester group (C=O) at a wavelength of 1712.57 cm^{-1}. Meanwhile, Figure 9 (b) shows that the peaks of the FTIR results of the polymer at 120°C and 165°C are almost the same. This means that the difference in polymerization temperature does not affect the type of functional groups in the resulting polymer. In addition to the ester group, several functional group peaks in the polymer sample include at wavelengths of 2926.71 cm^{-1} (C-H), 2855.41 cm^{-1} (C-H alkane), and 1178.63 cm^{-1} (C-OH alcohol).

The resulting polymer is in gel form. Determination of the molecular weight (MW) of the polymer was carried out by GPC analysis. Measurements were made by calibration using standard polymer solutions and internal calibration of the GPC equipment. After that, the BM of the polymer from this study was measured.

Table 2. Polyesterification reaction rate constant with the addition of a p-TSA catalyst.

T (°C)	*T* (K)	k_{cat}' ×10^3 (g.mmol^{-1}.min^{-1})
120	393.15	4.437
135	408.15	5.814
150	423.15	8.406
165	438.15	9.875

The analysis was carried out on two samples, namely the polymer produced from polyesterification at temperatures of 120°C and 165 °C. The complete chromatography results are presented in Table 3. Table 3 shows the dominant peak at this temperature occurs at a retention time of 11.005 minutes with an area percentage of around 59.89%. This peak has Mw and Mn values of around 548 and 525 Da. The average calculation results of the three peaks obtained Mw values of 728.47 Da; Mn of around 681.38 Da; and Z of around 1.4. While at a temperature of 165 °C, there are 4 peaks with areas of 25.52%; 26.60%; 37.95%; and 9.2%. At this temperature, the dominant peak occurs at a retention time of 11.007 minutes with Mw of 543 Da and Mn of around 522 Da. The average calculation of the four peaks produces Mw of around 1,131.80 Da; Mn of 1,049.63 Da; and Z of around 1.8. The two samples show a relatively low polydispersity value (<2), meaning that the polymers in each sample have a relatively narrow distribution. For monodisperse polymers (all chains with the same length), the polydispersity index (PDI) is 1. In general, synthetic polymers with narrow distributions and used for calibration have a PDI of around 1.02 - 1.10. Meanwhile, step-growth polymerization usually produces Mw/Mn values of around 2.0 (maximum conversion, > 99%) and chain-growth polymerization produces Mw/Mn values in the range of 1.5 - 20.

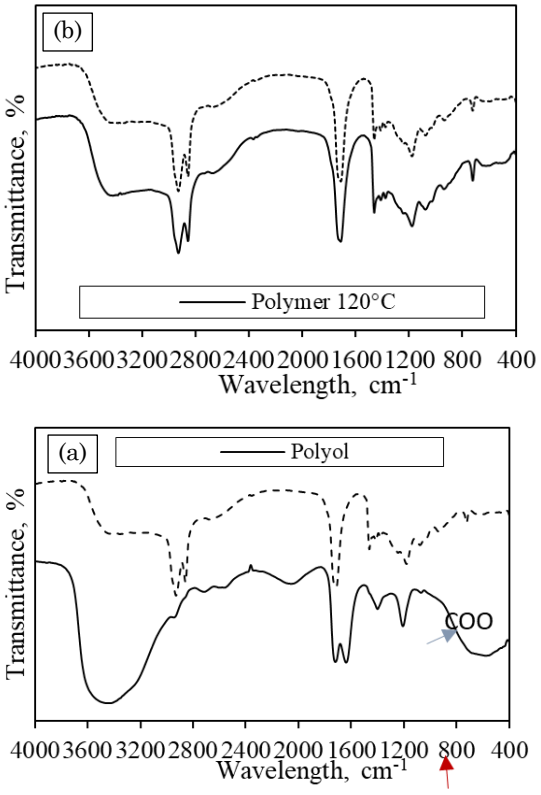

Figure 9. Results of FTIR analysis

4. Conclusions

Polyesters can be synthesized from tung oil-based polyols well**.** The polymerization was carried out in a 250 mL three-necked round-bottomed flask equipped with a magnetic stirrer, thermometer, and condenser. It is immersed in an oil bath to keep the reaction temperature stable. A vacuum pump was used to collect the produced moisture. Meanwhile, nitrogen gas (N_2) is ejecting oxygen from the reactor. Throughout the operation, the temperature and stirring speed were held constant for 6 hours. According to the results of the experiment, the best temperature for polyesterification was 150 °C. The reaction temperature has an inverse relationship with [OH] and [COOH], with the maximum conversion in the catalyst-free polyesterification being around 83.82% (against the OH cluster) and 94.95% (against the COOH cluster). According to the calculation's findings, polymerization without a catalyst yielded activation energies (*Ea*) of 27.2215 kJ/mol. Then, polymerization with catalyst decreased *Ea* value, which were around 26.4681 kJ/. Catalysts work by lowering the activation energy of a chemical reaction, thereby speeding up the reaction rate without being permanently involved in the reaction. In the context of collision factors, catalysts affect the way reactant molecules interact with each other during collisions.

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CRediT Author Statement

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Table 3. Molecular weight distribution and polydispersity

Temperature of polyesterification (°C)	*Peak*	Ret. Time	Area	% Area	Mn	Mw	Average Mn	Average Mw	Z
120	1	10.63	341008	29.35	1,178	1,286	681.38	728.47	1.4
	2	11.005	695573	59.87	525	548			
	3	11.435	125310	10.78	198	213			
165	1	10.382	260482	25.52	2,148	2,401	1,049.63	1,131.80	1.8
	2	10.612	271504	26.61	1,066	1,097			
	3	11.007	387388	37.95	522	543			
	4	11.433	101264	9.92	199	213			

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