

Synthesis and Kinetics of Hydrogenated Rosin Dodecyl Ester as an Environmentally Friendly Plasticizer

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Abstract: The plasticizer is an important polymer material additive. Non-toxic and environmentally friendly plasticizers are developed recently in order to decrease fossil fuel reserves, serious environmental pollution and the toxicity of phthalate esters. In this study, a new, efficient and environmentally friendly plasticizer of hydrogenated rosin dodecyl ester was prepared by an esterification reaction of hydrogenated rosin and dodecanol. The influences of different reaction conditions (including different catalysts, the catalyst concentration, the ratio of the reactants, reaction temperature, and reaction time) on the esterification yield are examined and discussed. Hydrogenated rosin dodecyl ester with 71.8% yield was synthesized under the optimized reaction conditions (1:0.8 molar ratio of rosin to dodecanol, 1 mol% tetrabutyl titanate concentration, and 210°C for 6 h). The esterification reaction is a second-order reaction, and kinetic calculations showed that the activation energy is 39.77 KJ·mol⁻¹. The structure of the hydrogenated rosin dodecyl ester was confirmed by FT-IR spectroscopy and ¹³C NMR spectrum. Besides, the thermal stability of target product (hydrogenated rosin dodecyl ester) was also tested by thermal gravimetric analysis (TGA), which showed a good thermal stability.

Keywords: Environmentally friendly plasticizer; hydrogenated rosin dodecyl ester; synthesis; kinetics study

1 Introduction

Plasticizers play an indispensable role in providing high-quality plastic products and are one of the most widely used plastic additives, with the largest worldwide output and consumption [1-3]. Phthalate esters have been widely applied in food, medicine and other industries as plasticizer [4]. Phthalate esters contain functional groups that include carboxylic esters, hydrocarbons, phosphate esters, ethers, halogenated alkanes, polyethylene glycol and epoxides [5]. Recent studies have focused on developing non-toxic and environmentally friendly plasticizers because of decreasing fossil fuel reserves, serious environmental pollution and the toxicity of phthalate esters [6]. Bio-based hyperbranched esters with excellent



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plasticizing properties, resistance to solvent extraction and low volatility have been synthesized from castor oil [7-8]. A novel environmentally friendly plasticizer applied for PVC blends has been synthesized and showed excellent thermal stability and high migration resistance [9]. In these studies, biomass resources have been used to synthesize non-toxic, environmentally friendly, biodegradable bio-based plasticizers with excellent properties [10-12].

Rosin is an abundant, renewable natural resin composed of 90% resin acid and 10% neutral compounds [13]. Rosin has a large hydrogenated phenanthrene ring that has similar molecular rigidity to cyclic aliphatic or aromatic compounds [14-16]. Rosin acid contains a carboxylic acid group and a conjugated carbon-carbon double bond that can be modified by esterification, Diels-Alder addition, and saponification reactions [17-19]. The rosin-based products obtained from these reactions can serve as alternatives to petroleum-based cyclic aliphatic or aromatic monomers for the synthesis of diglycidyl acrylpimaric acid ester, dehydroabietic acid and maleic anhydride, precursors to fine chemicals [20-21]. Hydrogenated rosin products have been used to prepare fine chemicals, including medicines [22-23]. However, to the best of our knowledge, the hydrogenated rosin dodecyl ester has been only rarely studied.

In this work, hydrogenated rosin dodecyl ester was prepared via the esterification reaction of dodecanol and hydrogenated rosin under solvent-free conditions (Fig. 1). The reaction time, reaction temperature, catalyst type and other significant factors were optimized to obtain the optimum reaction conditions and the kinetics of the reaction were studied. The structure and thermal stability of the hydrogenated rosin dodecyl ester were also tested.

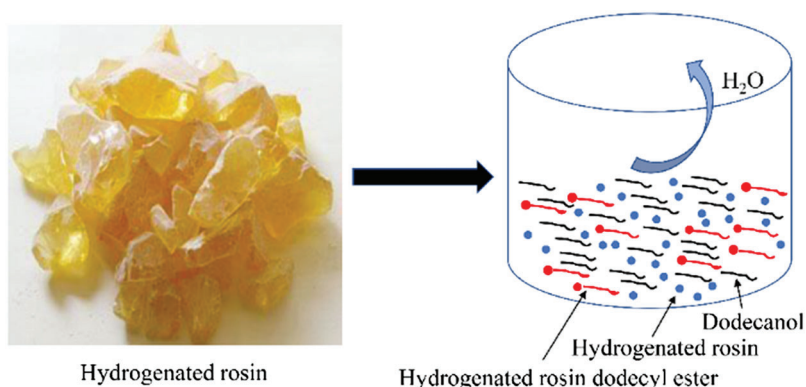


Figure 1: Schematic representation of hydrogenated rosin dodecyl ester

2 Experimental

2.1 Materials

Hydrogenated rosin was supplied by Hunan Pine Forest Technologies Co. Ltd. Tetra-butyl titanate, dodecanol, sodium hydroxide and zinc oxide were supplied by Aladdin Chemical Reagent Co. Ltd. All chemicals were used without further purification.

2.2 Synthesis of Hydrogenated Rosin Dodecyl Ester

An appropriate amount of hydrogenated rosin and dodecanol were placed in a 250 ml flask. When the temperature reached the desired reaction temperature, the tetra-butyl titanate catalyst was slowly added dropwise. Then the mixture was maintained at the reaction temperature for a fixed time under a nitrogen atmosphere. Hydrogenated rosin dodecyl ester was obtained from the above experiment.

2.3 Characterization and Measurements

FT-IR: Fourier transform infrared (FT-IR) spectra were carried out on a Thermo Scientific Nicolet IS10 spectrometer (Nicolet, USA) by ATR (attenuated total reflectance). The spectra were recorded over the range 4000-600 cm^{-1} at 4 cm^{-1} resolution and averaged over 16 scans per sample.

TG: Thermal stabilities of the samples were determined on a TG209F1 (Netzsch, Germany). The samples were heated from 25°C to 800°C at a rate of 10°C min^{-1} under a nitrogen atmosphere.

Calibration of the acid value of the hydrogenated rosin: The acid value of the hydrogenated rosin was determined by acid-base titration. Hydrogenated rosin (2.0 g) was completely dissolved with absolute ethanol (50 ml) in a conical bottle (250 ml). After 3-5 drops of a phenolphthalein indicator solution was added, the hydrogenated rosin-ethanol solution was titrated with a KOH standard solution until the color changed to light pink. Then, the consumption of KOH required to maintain the pink color for 30 seconds was recorded as the end point of the acid value calibration. The formula for calculating the acid value of the hydrogenated rosin is as follows:

$$Y = \frac{(v_1 - v_2) \times c \times 56.1}{m} \quad (1)$$

where Y is the acid value of the hydrogenated rosin (mg/g), v_1 is the volume of the KOH standard titration solution consumed by the sample (ml), v_2 is the volume of the KOH standard titration solution consumed in a blank test (ml), c is the concentration of KOH in the standard titration solution (mol/L), m is the mass of the sample (g) and 56.1 is the molar mass of KOH (g/mol).

The yield of esterification product:

$$x = 1 - \frac{z}{y} \quad (2)$$

x is the yield of the esterification of the hydrogenated rosin dodecyl ester, z is the acid value of the sample after the reaction (mg/g) and y is the acid value of the sample before the reaction (mg/g).

3 Results and Discussion

3.1 Effect of Different Catalysts on the Esterification

Homogeneous and heterogeneous catalysts such as HNO_3 , H_2SO_4 , ZnO and tetrabutyl titanate were tested in the catalytic esterification reaction to obtain good yields of the ester with higher selectivity. The esterification of hydrogenated rosin and dodecanol was performed with a reaction temperature of 210°C, a reaction time of 6 h, a molar ratio of hydrogenated rosin to dodecanol of 1:0.8, and a molar ratio of catalyst to hydrogenated rosin of 1%. The results with different catalysts are shown in [Tab. 1](#). The lowest esterification yield, obtained without a catalyst, was 21.8%. This is due to the high activation energy required for the esterification reaction, which arises from the high steric hindrance of hydrogenated rosin

Table 1: The effect of different catalysts on the esterification

Sample	Catalysts	Catalyst concentration (mol%)	Esterification yield (%)
1	–	0	21.8
2	HNO_3	1	70.3
3	H_2SO_4	1	54.7
4	ZnO	1	70.0
5	Ti ($\text{C}_4\text{H}_9\text{O}$) ₄	1	71.8

(due to tertiary carbon atoms) [24]. Thus, the selection of a highly active catalyst is very important for the esterification of hydrogenated rosin. The esterification yields with different acid catalysts were 70.3% and 54.7% with HNO_3 and H_2SO_4 , respectively. However, the use of strong acids causes serious environmental pollution due to the large amount of wastewater requiring post-treatment and also causes equipment corrosion [25]. An esterification yield of 70.0% was also obtained using ZnO as a catalyst. However, the high reaction temperature and long reaction time required, together with the high toxicity of the ZnO catalyst, limits its use [26].

The highest esterification yield obtained was 71.8% using tetrabutyl titanate as the catalyst. This catalyst avoids both equipment corrosion and environmental pollution. Homogeneous catalysts have better catalytic activities than heterogeneous catalysts because they have better contact with the reactants. With tetrabutyl titanate as the catalyst, the esterification reaction mechanism is as follows (Fig. 2) [27]. The carbonyl group of the hydrogenated rosin binds to the titanium(IV) ion, transferring electron density from the carbonyl group to the titanium ion. This makes the carbon atoms in the carbonyl group more susceptible to nucleophilic attack. After the nucleophilic addition of dodecanol, a transition state with four bonds to the carbon center is formed. Then the $\text{C}-\text{O}$ bond is broken and the ester group forms. Finally, the titanium ion dissociates from the carbonyl group, thus completing the catalytic reaction cycle. In summary, tetrabutyl titanate was selected as the optimum catalyst.

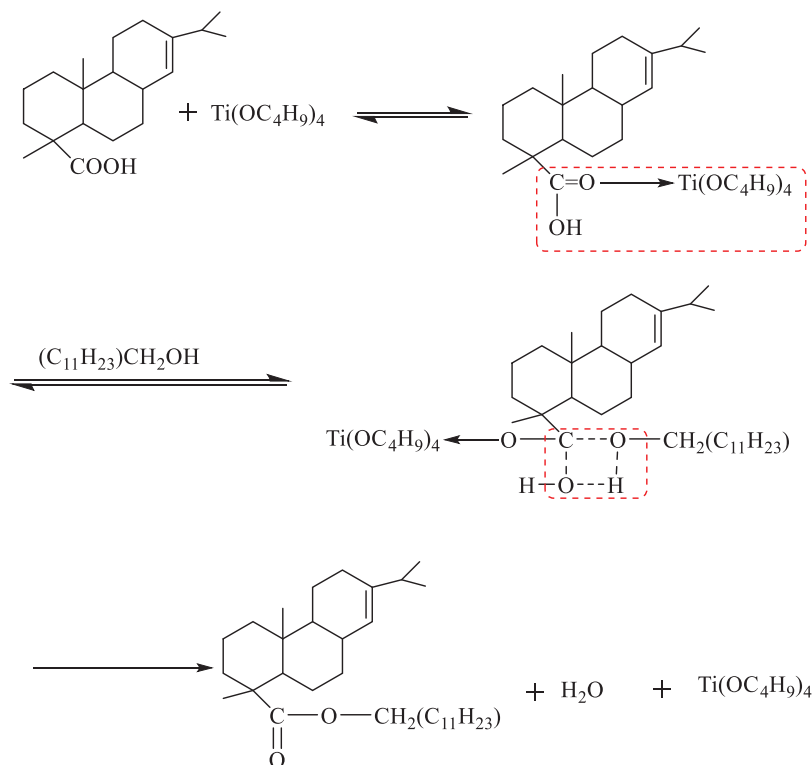


Figure 2: The mechanism of the esterification reaction

3.2 Effect of the Catalyst Concentration on the Esterification

The esterification of hydrogenated rosin and dodecanol was performed with a reaction temperature of 210°C , a reaction time of 6 h, a molar ratio of hydrogenated rosin to dodecanol of 1:0.8, and different catalyst concentrations. Higher concentrations of the tetrabutyl titanate catalyst resulted in higher yields

from the esterification, indicating that the reaction rate of rosin acid is faster (Tab. 2). The activation energy of the esterification also decreased in the presence of the tetrabutyl titanate catalyst. When 0.5 mol% tetrabutyl titanate was used, the yield of the esterification was 57.9%, because the insufficient catalyst concentration resulted in an incomplete esterification. The yield of the esterification reached 71.8% when 1 mol% tetrabutyl titanate was used. If more catalyst was used, no obvious changes in the yield of the esterification were observed (the yield remains ~70%) because the reaction is reversible. In summary, the appropriate amount of catalyst is 1 mol%, which optimizes the yield of the esterification, environmental protection and cost.

Table 2: The effect of the catalyst concentration on the esterification

Sample	Molar ratio of the reactants	Catalyst concentration (mol%)	Temperature (°C)	Time (h)	Esterification yield (%)
6	1:0.8	0	210	6	21.8
7	1:0.8	0.5	210	6	57.9
8	1:0.8	1	210	6	71.8
9	1:0.8	1.5	210	6	68.5
10	1:0.8	2	210	6	73.0

3.3 Effect of the Ratio of the Reactants on the Esterification

The esterification of hydrogenated rosin and dodecanol was performed with a reaction temperature of 210°C, a reaction time of 6 h, a molar ratio of the catalyst to hydrogenated rosin of 1 mol%, and different ratios of hydrogenated rosin to dodecanol (Tab. 3). When the molar ratio of hydrogenated rosin to dodecanol was 1:0.8, the yield of the esterification was maximized at 71.8%. If the molar ratio was lower than 1:0.8, the yield of the esterification decreased significantly, to less than 50%. When the molar ratio was higher than 1:0.8, the yield of the esterification remained at approximately 70%. These experimental results disagree with what has been previously reported in the literature. This suggests that the molar ratio of dodecanol to the hydrogenated acid has a threshold value. The concentration of the hydrogenated acid in the reactant is lowered by excess dodecanol, which affects the yield of the esterification. In summary, the optimum molar ratio of hydrogenated rosin to dodecanol is 1:0.8.

Table 3: The effect of the ratio of the reactants on the esterification

Sample	Molar ratio of the reactants	Catalyst concentration (mol%)	Temperature (°C)	Time (h)	Esterification yield (%)
11	1:0.6	1	210	6	40.3
12	1:0.7	1	210	6	45.4
13	1:0.8	1	210	6	71.8
14	1:0.9	1	210	6	66.2
15	1:1.0	1	210	6	68.4

3.4 Effect of the Reaction Temperature on the Esterification

The esterification of hydrogenated rosin and dodecanol was performed using a reaction time of 6 h, a molar ratio of hydrogenated rosin to dodecanol of 1:0.8, a molar ratio of catalyst to hydrogenated rosin of

1% and different reaction temperatures. Tab. 4 shows that when the reaction temperature is relatively low, the catalytic reaction is slow. For example, the yield of the esterification was 51.2% and the esterification was incomplete at 190°C. When the temperature was increased, the esterification reaction was more complete. When the reaction temperature was 220°C, the highest yield of 73.3% was obtained from the esterification. If the reaction temperature was too high, the yield of the esterification decreased. This may be due to the decarboxylation of rosin acid at high temperatures or the evaporation of a small amount of dodecanol. The yields of the esterification of hydrogenated rosin with dodecanol at 210°C and 220°C were similar. In summary, to conserve energy, the optimal reaction temperature is 210°C.

Table 4: The effect of reaction temperature on esterification

Sample	Molar ratio of the reactants	Catalyst concentration (mol%)	Temperature (°C)	Time (h)	Esterification yield (%)
16	1:0.8	1	190	6	51.2
17	1:0.8	1	200	6	69.9
18	1:0.8	1	210	6	71.8
19	1:0.8	1	220	6	73.3
20	1:0.8	1	230	6	61.0

3.5 Effect of Reaction Time on Esterification

The esterification of hydrogenated rosin and dodecanol was performed with a reaction temperature of 210°C, a molar ratio of hydrogenated rosin to dodecanol of 1:0.8 and a molar ratio of catalyst to hydrogenated rosin of 1% for different reaction times (Tab. 5). With increasing reaction time, the yield of the esterification reaction increased (the esterification rate also increased gradually). The yield of the esterification increased from 51.8% to 71.8%. Further increasing the reaction time significantly reduced yield of the esterification. The progress of the esterification reaction is related to the reaction time. The reaction reaches an optimum yield after 6 h due to the increased amount of catalytic active sites that promote the catalytic esterification. In summary, a reaction time of 6 h is suitable.

Table 5: The effect of the reaction time on the esterification

Sample	Molar ratio of the reactants	Catalyst concentration (mol%)	Temperature (°C)	Time (h)	Esterification yield (%)
21	1:0.8	1	210	4	51.8
22	1:0.8	1	210	5	60.0
23	1:0.8	1	210	6	71.8
24	1:0.8	1	210	7	67.1
25	1:0.8	1	210	8	71.7

3.6 Kinetics of the Esterification Reaction

The change in the acid value of the esterification reaction was measured under the optimized reaction conditions and used to plot the C-T curve shown in Fig. 3 (where C is the acid value of the reaction system). The acid value of the system first decreased and then stabilized over time. The experimental data

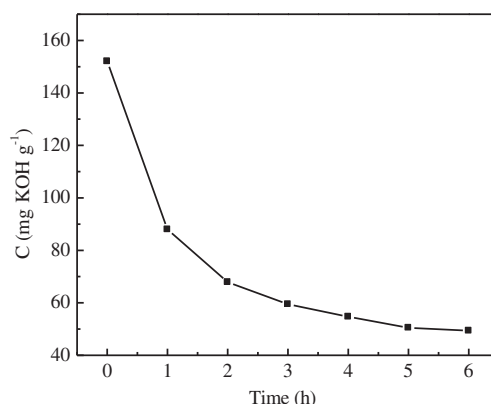


Figure 3: Relationship between the acid value and time

Table 6: Reaction kinetics data [24-25]

Time (h)	Acid value	$c_{A0}-c_A$	$\ln(c_{A0}/c_A)$	$1/c_A-1/c_{A0}$
0	152.0462	0	0	0
1	87.9736	64.07261	0.547148	0.00479
2	67.88779	84.15842	0.806328	0.008153
3	59.47195	92.57426	0.93868	0.010238
4	54.70297	97.34323	1.022266	0.011704
5	50.49505	101.5512	1.102309	0.013227
6	49.37294	102.6733	1.124782	0.013677

Table 7: Kinetic fitting data and correlation coefficients

Reaction order	Calculated formula	k	R ²
Zero order	$y = 14.149x + 35.036$	14.149	0.6951
First order	$y = 0.1103x + 0.5376$	0.1103	0.8948
Second order	$y = 0.0022x + 0.0022$	0.0022	0.9125

were fit with zero order, first order, and second order kinetics equations (Tab. 6) and the kinetic results obtained are shown in Tab. 7. From Tab. 7, the best value of the correlation coefficient R^2 is 0.9125. This suggests that the reaction is a second order reaction.

The second-order reaction rate equation can be simplified to $(1/c_A - 1/c_0) = kt$. Using this equation, the reaction rate constant (k) can be obtained at different temperatures (Fig. 4). The k values are $0.0023 \text{ mgKOH} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$, $0.0020 \text{ mgKOH} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$, $0.0022 \text{ mgKOH} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ and $0.0011 \text{ mgKOH} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$, respectively.

The activation energy of the esterification reaction (E_a) can be obtained using the Arrhenius Eq. (3). From the plot of $\ln k$ versus $1/T$, E_a was $39.77 \text{ KJ} \cdot \text{mol}^{-1}$ (Fig. 5).

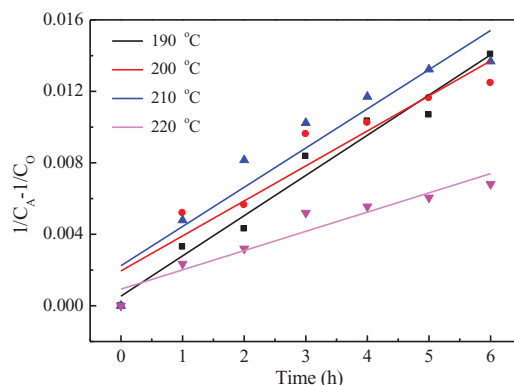


Figure 4: The relationship between $(1/c_A - 1/c_0)$ and the time at different temperatures

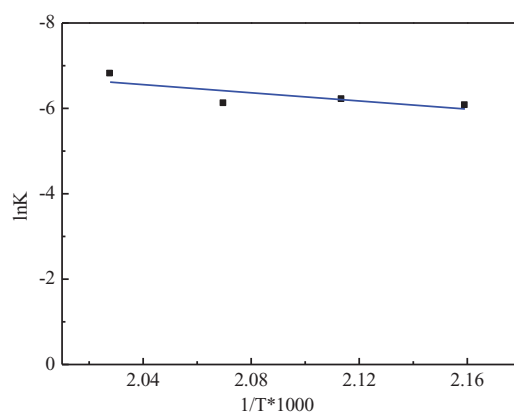


Figure 5: Relationship between $\ln k$ and $1/T$

$$\ln k = \frac{-Ea}{RT} + c \quad (3)$$

3.7 FT-IR Analysis

The strong absorption peak at 1688 cm^{-1} can be assigned to the carboxyl $\text{C}=\text{O}$ stretching vibration of hydrogenated rosin. The new characteristic absorption peak at 1730 cm^{-1} belongs to the ester group of the hydrogenated rosin dodecyl ester product. These vibrations show that the carboxyl group reacts with hydroxyl groups to form the target product (Fig. 6).

3.8 ^{13}C of NMR Analysis

In ^{13}C NMR spectrum in Fig. 7, the signal at $\sim 30 \text{ ppm}$ can be assigned to a methyl group. The characteristic peak at 65 ppm corresponds to the $\text{O}-\text{C}$ in the dodecanol chain. The characteristic peak for the ester group occurs at 178 ppm and the peak for the carbon-carbon double bond occurs at 125 ppm .

3.9 Thermal Properties

The thermal degradation of hydrogenated rosin dodecyl ester was investigated by TGA, as shown in Figs. 8 and 9. In the TGA curve, the 5% mass loss temperature is 220°C . In the DTG curve, the maximum

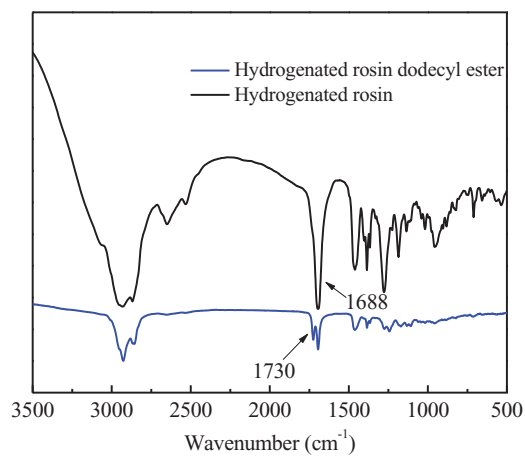


Figure 6: FT-IR characterization of hydrogenated rosin dodecyl ester

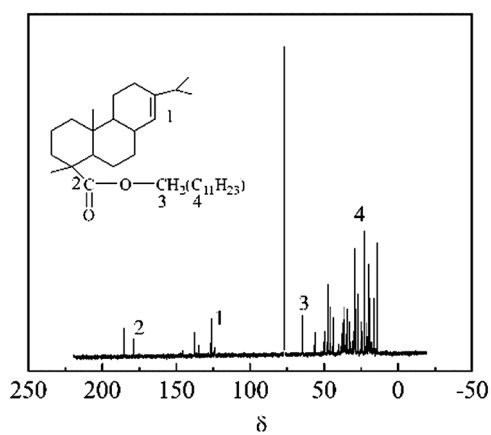


Figure 7: ¹³C of NMR characterization of hydrogenated rosin dodecyl ester

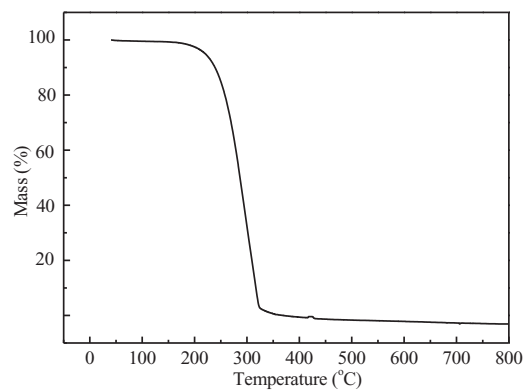


Figure 8: The TG curve of hydrogenated rosin dodecyl ester

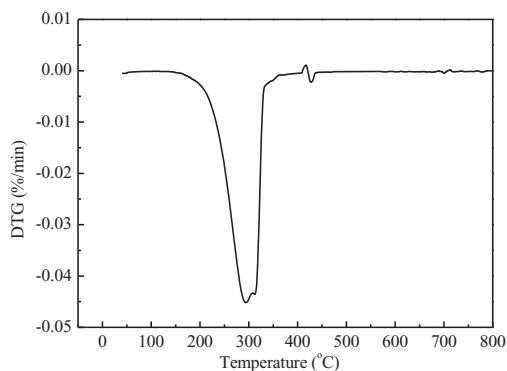


Figure 9: The DTG curve of hydrogenated rosin dodecyl ester

weight loss rate is observed at 287°C. These data show that hydrogenated rosin dodecyl ester has excellent thermal stability. Hydrogenated rosin dodecyl ester can be used as a new green plasticizer with good temperature resistance because the processing temperature of PVC resin is generally in the range of ~150–180°C.

4 Conclusion

In summary, hydrogenated rosin dodecyl ester was prepared by an esterification reaction of hydrogenated rosin and dodecanol. The optimized experimental conditions for the esterification reaction were a 1:0.8 molar ratio of hydrogenated rosin to dodecanol with 1 mol% tetrabutyl titanate as the catalyst at 210°C for 6 h. The esterification of hydrogenated rosin dodecyl ester is a second-order reaction, with an activation energy of 39.77 KJ·mol⁻¹. The TGA analysis showed that hydrogenated rosin dodecyl ester has good thermal resistance and can be considered as a green plasticizer.

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Conflicts of Interest: The authors declare that they have no conflicts of interest to report regarding the present study.

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