Synthesis and Characterization of Water Soluble Rosin-Polyethylene Glycol 1500 Derivative

P. Kanlaya, W. Sumrit, and P. Amorn

***Abstract*—This research aims to synthesize and characterize of rosin-polyethylene glycol derivatives from natural rosin and polyethylene glycol 1500 (PEG1500). In this research, reaction conditions for the synthesis of rosin-PEG derivatives such as catalyst type, catalyst concentration, reaction temperature and etc. were optimized. Chemical and physical properties of water soluble rosin (WSR) were characterized using FT-IR, ^{13}C-NMR, DSC, and GPC. It was found that water soluble rosin-PEG derivatives were successful synthesized from natural china rosin and PEG using 2% ZnO as catalyst, 2:1 molar ratio of rosin: PEG at 250 ^{O}C for 9 hours. The obtained rosin-PEG1500 derivative were completely soluble in water and rosin-PEG1500 derivative showed melting point at 40.6 ℃.**

***Index Terms*—Water soluble rosin, polyethylene glycol 1500, esterification, zinc oxide.**

I. Introduction

The development of a sustainable material is one of the most pressing issues for future generations. Energy production and plastic manufacturing produced from fossil fuel has finite availability. Within the next century, it will be nearly depleted. The environmental concerns, along with depleting oil reserves, have led to an increased interest in the development of green material derived from renewable natural resources [1].

One of most interested renewable material is rosin. Rosin or colophony is a renewable, abundant, natural material derived from pin tree and wildly used in the paper, coating, printing ink, polymer, food industries as well as a precursor for flux in soldering [2]. The major compositions of rosin include resin acids represented acids or dimmers or as anhydrides by general formula $C_{20}H_{30}O_2$ that are present as free. They are monocarboxylic acids of alkylated hydrophenanthrene; abietic acid constitutes the principal resin acid. [3], [4]. It is soluble in alcohol, ether, benzene and chloroform but insoluble in water Polyethylene glycol (PEG) or poly (ethylene oxide) is petroleum base polymer represent water-soluble mono hydroxy alcohols. These are water-soluble polymers used as base in ointments and suppositories, as plasticizer in film coating, as auxiliary emulsifiers [4], as flux vehicle in WSFs for electronic industrial [5], [6], etc**.** In the previous study, modification of rosin also improves its safety and stability. The two reactive sites of resin acids – carboxyl group and conjugated double bond – were utilized to synthesize the present ester-adduct derivatives via esterification reaction. Nande *et al.* (2006, 2007, 2008), Morkhade *et al.* (2008) synthesized rosin ester derivatives by reacting rosin with PEG, maleic anhydride (MA). Zinc dust was used as a catalyst. The derivatives soluble in organic solvents. Aqueous solubility was pH dependent and investigated as drug delivery material. Rosin poly (oxyethylene) ester 4,5-dihydroimidazole maleate adduct (RIMA-PEG) was synthesized as corrosion inhibitor for carbon steel [8].

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Therefore the purpose of this research was to synthesize and study properties of rosin-polyethylene glycol derivatives from natural rosin and polyethylene glycol (PEG). Catalyst types, catalyst concentrations, reaction temperatures, reaction times, catalyst ratio, PEG type were studied and investigated.

II. Experimental Details

A. Material

Rosin (WW grade) was purchased from Petch Thai Chemical Co, Ltd. and imported from China. PEG 1500, zinc dust, zinc oxide and tin chloride anhydrous were purchased from Merck Co., Ltd.. All the other chemicals were used synthesis grade and were used as received.

B. Study on Optimized Conditions for Synthesis Reaction of Rosin Ester Derivatives

China rosin (WW grade) was placed in a boiling flask 100 ml. and heated at 100–150 ℃ on a heating mantle with stirrer. PEG1500 was mixed with rosin solution using magnetic bar inside set at 750 rpm. The temperature of the mixture was studied at 100–250 ℃ until the completion of reaction. In this research, zinc dust, zinc oxide and tin chloride were selected and varying concentration of catalyst was study at 0.5-3.0 %. The reaction completion was measured acid number by KEM Automatic Potentiometric Titrator (AT-510) with 0.1 molar of KOH and use this value for conversion calculation. The molten of the water soluble rosin was poured on aluminum foil cup, allowed to solidify and used as sample for testing.

C. Characterization of Rosin Ester Derivatives

Melting point of derivatives was determined by NETZSCH DSC240F1 Phoenix 240-12-0322-L. FT-IR spectroscopy (Perkin Elmer, Spectrum One) was used to determine the functional group of the water soluble rosin. ^{13}C NMR spectroscopy (Bruker Avance III HD 500 MHz spectrometer)

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was used to confirm ester bonding of rosin derivatives. Molecular weights and polydispersity were measured using gel permeation chromatography with a differential refractometer (model RI-10A; Shimadzu). XRF spectroscopy was used to confirm the present of Zn in the synthesized product.

III. Results and Discussions

A. Optimized Conditions for Synthesis Reaction of the Esterification Reaction

The target of this reaction was the carboxylic group of rosin reacted with hydroxyl group of PEG to form rosin-PEG derivatives and water via esterification reaction. The sequence of reaction taking abietic as model component is given in Fig. 1. This reaction is reversible reaction that leads to formation of variety products. Products with high ester yield can be obtained either by using catalysts or by use of one of reactant (rosin, PEG) in large excess or by removal of water by increase temperature. Therefore, in this research was to study the effect of catalyst type, catalyst concentration, rosin concentration, reaction temperatures and reaction time on rectification reaction. Reaction conversion was determined by acid value of reactor.

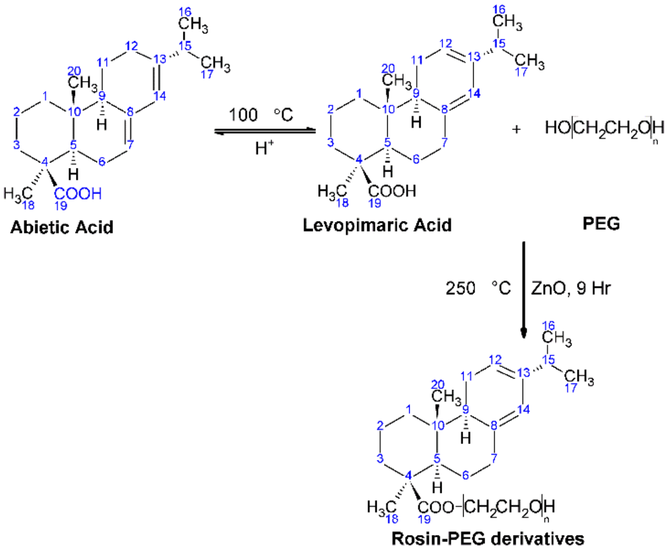

Fig. 1. Reaction scheme of water soluble rosin synthesis.

B. Study of Influence of Catalyst Type on the Esterification Reaction

In this research Zn-dust, ZnO and Tin chloride were selected as catalyst study for esterification reaction of rosin and PEG. Fig. 2 shows conversion percentile of reaction used Zn-dust, ZnO and Tin chloride. Rate of reaction was significantly increased by all catalysts. Zinc oxide showed the most effective catalyst as it resulted in the highest conversion of ester at 5 hours due to lewis acid performance of this catalyst however zinc dust did not, it may suggest that zinc cation is more readily dissolved from oxide surface into the reaction media comparing with metallic Zn [9]. Even though zinc oxide and tin chloride are lewis acid but zinc oxide showed higher reaction rate than tin chloride due to moisture and temperature stable of zinc oxide and the result showed consistence with previous studied [10], [11]. Therefore zinc oxide was selected for esterification reaction.

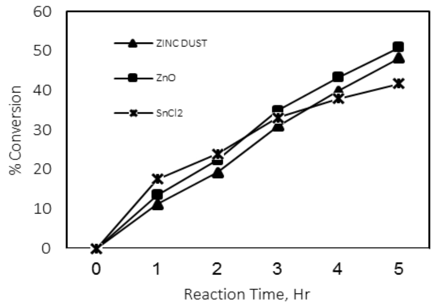

Fig. 2. Conversion (%) of reaction versus time for the esterification reaction of rosin and PEG1500 using Zn dust, $SnCl_2$ and ZnO as catalysts using 0.5 % of catalyst, 1:1 of rosin/PEG @ 250OC for 5 hrs.

C. Study of Influence of Catalysts Concentration on the Esterification Reaction

The Fig. 3 shows conversion percentage of reaction and acid value versus catalyst concentration (%) for the esterification reaction of PEG1500 and 0.5% zinc oxide at 250 ℃ for 5 hours. The data showed that when increased concentration of catalyst from 0.5% to 2.0% reaction conversion was increased from 30.2 % to and 69.4 % but decreased to 67.0 % when catalyst concentration was increased up to 3.0 %. It can suggest that the increases of the catalyst concentration have a noticeable effect on the conversion rate of the rosin acid into ester derivatives. This fact can be attributed to higher number of molecules of substrate activated by polarization of the carbonyl, in presence of Zn^{2+} catalyst. Thus, the nucleophilic attack by hydroxyl of PEG becomes more favorable and consequently, an increase on the formation of ester was observed. This result shows consistence with the previous study [12], [13]. Therefore the optimum catalyst concentration was 2 % of rosin content.

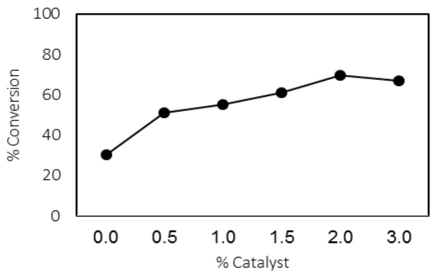

Fig. 3. Conversion (%) of the esterification reaction between rosin and PEG1500 using catalyst concentration 0% to 2 % @ 250OC for 5 hrs.

D. Study of Influence of Temperature on the Esterification Reaction

In this study, reaction temperature at 100, 150, 200, 225, 250 ^{O}C for 5 hours was selected for investigation of reaction temperature effect. Table II shows the summary of test result of rosin derivatives at 100, 150, 200, 225, 250 ℃ for 5 hours. The results shows that, the acid value of reactants did not change at 100 ℃ and dropped when reaction temperature was increased to 150, 200, 225, 250 ℃. From data it can conclude that at 100 ℃ reaction of rosin and PEG was not occurred and increased when reaction temperature was raise due to water molecule was faster removed and materials were converted into esters of rosin. Water solubility of synthesized product was higher at 250 ℃. This result shows consistence with the previous study [13]-[15]. Therefore the optimum reaction temperature was 250 ℃.

TABLE I: CONVERSION PERCENTAGE, ACID VALUE AND WATER SOLUBILITY OF REACTION AT TEMPERATURE 100, 150, 200, 225, 250 ℃.

Reaction Temperature, °C	Acid Value start	Acid Value 5 hr, (mg. KOH/g)	% conversion	Water solubility, g/ml
100	46.5	47.6	0.0	0.35
150	47.02	43.9	6.5	0.24
200	49.0	44.92	8.2	0.00
225	49.56	41.3	16.7	0.01
250	47.4	16.4	65.5	0.96

E. Study of Influence of the Rosin/PEG Ratio on the Esterification Reaction

The rosin to PEG molar ratio is one of the important parameter that affecting the rosin acid conversion to rosin ester derivatives. The effect of rosin to PEG molar ratio molar ratio on conversion of rosin acid was investigated at fixed temperature at 250 ℃ and catalyst concentration at 2%. Fig. 4 represent rate of esterification reaction at the various concentration ratio of rosin: PEG. It was found that the reaction rate of rosin acid to rosin ester derivatives was 15.72 mmol.hr^{-1} at 2:1 molar ratio of rosin to PEG. The optimum molar ratio of rosin to PEG was 2:1.

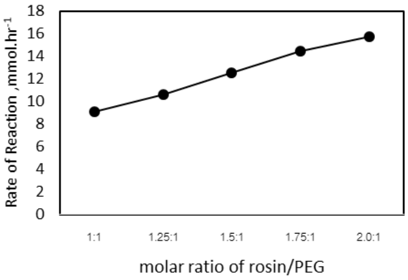

Fig. 4. Rate of reaction of esterification reaction using difference rosin/PEG ratio using ZnO 2% @ 250 ℃ for 5 hrs.

Fig. 5. Conversion (%)of esterification reaction using ZnO 2%, 2:1 of rosin: PEG1500 @ 250 ℃ for 10 hrs.

F. Study of Influence of the Rosin/PEG Ratio on the Esterification Reaction

The highest of conversion of rosin and PEG to rosin ester derivative is expectation of this study therefore increasing time was investigated. Effect of reaction time to conversion of esterification reaction is represented in Fig. 5. The result showed that when increased reaction time from one to eight hours reaction conversion was significantly increased and seems constant from nine to ten hours. And reaction time at nine hours was suggested to optimum reaction time with 95 % conversion.

G. Characterizations of Rosin Derivatives

In this study, FT-IR and ^{13}C NMR spectroscopy were the technique for characterization and confirmation of ester bond formation of rosin ester derivatives. Fig. 6 presents the IR spectra of rosin, PEG, rosin derivative at 0 hour, 5, hours and 10 hours respectively. The IR spectra of China rosin, C=O stretching at 1690 cm^{-1} and O–H stretching at 3568 cm^{-1} indicated that the presence of carboxylic acid in rosin. The IR spectra of derivatives at 0 hour show C=O stretching ratio at 1690 cm^{-1} higher than 1721 cm^{-1} and reduced when the reaction time was increased suggested that the conversion of acid to ester was occurred and increased when increasing reaction time. This is consistent with the previous study [14]. These results suggest that ester group presented in all kinds of rosin-PEG derivatives. The ^{13}C NMR spectra of all rosin-PEG derivatives were presented in Fig. 8, the chemical shift around 180 ppm support that the ester bond created in all rosin-PEG derivatives and these findings are consistent with the previous study [16]-[18]. From all results, the sequence of reaction can be proposed as given in Fig. 1.

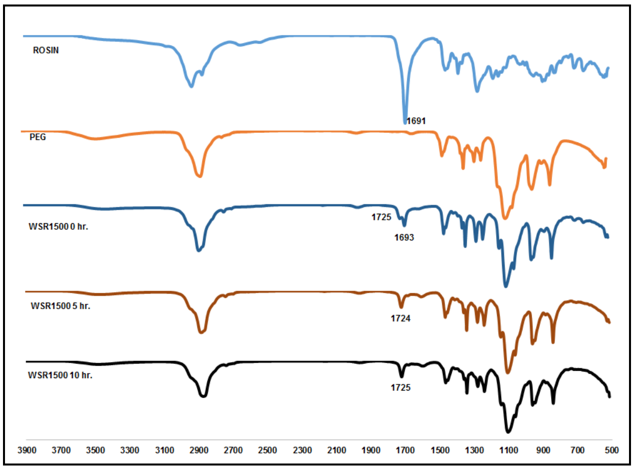

Fig. 6. Infrared spectra of China rosin, PEG and the Rosin-PEG1500 derivative at 0, 5, 10 hrs.

H. Characteristic of Water Soluble Rosin-PEG Derivatives

Fig. 7 presents the DSC spectra of rosin-PEG derivatives, it appears that the melting point of derivatives was decreased from native rosin and increase when molecular weight of PEG increased. Water solubility of all rosin-PEG derivatives were 100%, it can suggested that the carboxylic group in rosin reacted with hydroxyl group in PEG1500 and yielded ester bond. These effected to increasing water solubility property of native rosin therefore rosin-PEG derivatives were dissolved in water via hydroxyl group in PEG molecule.

Fig. 9 shows XRF spectra of Zn content in rosin-PEG derivatives. This data indicated that Zn still remained in the final synthesized product and dissolve in water. The results showed that % Zn contained in rosin-PEG1500 derivatives was 0.606%. It may assume that ZnO used as catalyst was changed from ZnO in to acetate form which dissolve in water.

The physical and chemical properties of rosin, PEG and WSRs are summarized in Table II. From the results shows that all kind of PEGs showed excellent water solubility and melting temperature of WSR1500 was 40.6 ^{O}C and lower than native rosin and PEG1500. From this result it can suggest than melting point of derivative was affected from rosin content and melting point of PEG. This result shows consistent with previous study [4], [14], [19].

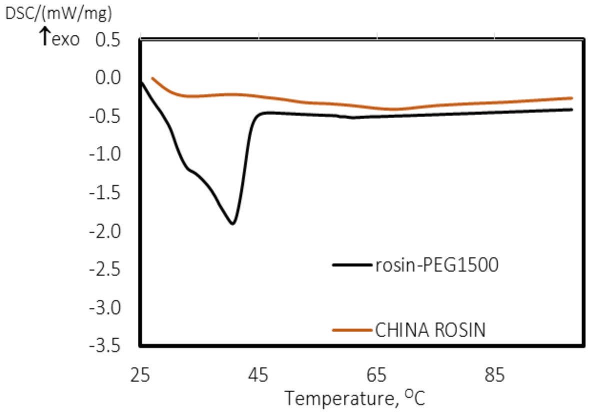

Fig. 7. DSC spectra of China rosin and rosin-PEG 1500 derivatives.

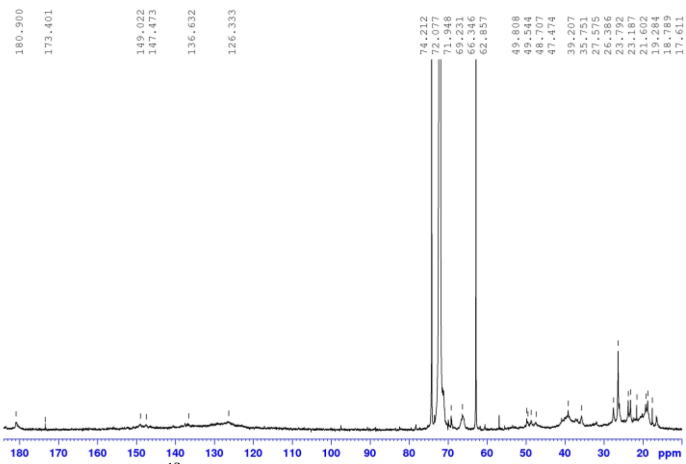

Fig. 8. ^{13}C-NMR spectra of rosin-PEG 1500 derivatives.

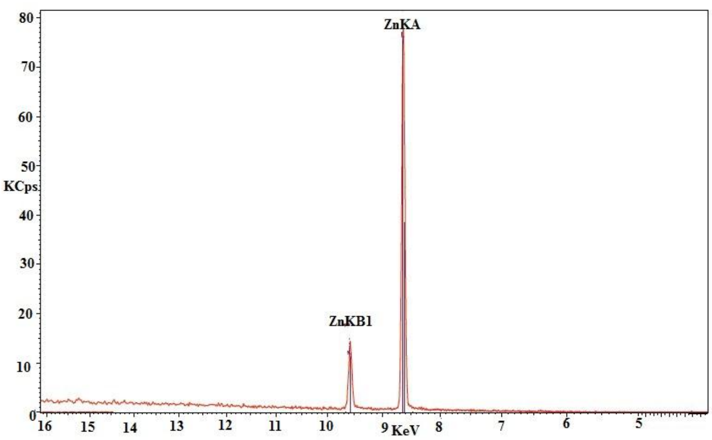

Fig. 9. XRF spectrum of Zn in rosin-PEG 1500 derivatives.

TABLE II: PHYSICAL AND CHEMICAL PROPERTIES OF WSRS

	Items	China Rosin	PEG1500	WSR1500
1.	Appearance	Yellow Solid	Yellow Solid	Dark brown semi-solid
2.	Melting point (^{O}C)	67.8	45.9-48	40.6
3.	Weight-A.M.W. (Mw)	302	1570	1647
4.	Water solubility	Insoluble	Soluble	Soluble
5.	Acid value (mg. KOH/g)	170.4	0	2.97

IV. CONCLUSION

Rosin-PEG 1500 derivatives were successful synthesis from natural rosin and PEG using ZnO 2% as catalyst, 2 molar of rosin at 250 ^{O}C for 9 hours. This derivatives were completely soluble in water then we can call water soluble rosin (WSR). WSR1500 showed melting point at 40.6 ^{O}C but lower than native rosin. Acid value was 2.97 mg. KOH/g and 95 % conversion at 9 hours. A.M.W. (Mw) of this derivatives were 1647.

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