

Preparation And Characterization of Alkyd Resin Polymer of Vegetable Oil Under the Influence of a Catalyst and A Kinetic Study of Its Polymerization

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Abstract

The study included the preparation of a polymer (alkyd resin) in two steps: the first is the preparation of monochlorides from the reaction of glycerine with castor oil in the presence of catalysts (Pb2O3, LiOH) and at a temperature (150 °C). A catalyst (CaCO3) and a range of temperatures (210, 200, 190, 180, 170) °C. The polymer was studied and identified by: infrared spectroscopy (FTIR) and proton nuclear magnetic resonance (1HNMR), and adhesiveness test. The molecular weight of the polymer was calculated by means of gel permeation chromatography (GPC) and calculated by means of viscometric viscosity through the graph of the polymer. The kinetics of the polymerization reactions was studied by tracking the decrease in the acid value and the amount of water removed from the reaction medium of the polymer prepared using the catalyst (CaCO3). The activation energy (Ea) and frequency coefficient (A) were calculated from the Erinus equation. And calculating thermodynamic functions (ΔH° , ΔS° , ΔG°).

Keywords

Alkyd Resins, Polymerization of Castor Oil, Effect of The Catalyst on The Polymerization Reaction, FTIR, 1HNMR, Activation Energy Ea.

Alkyd resins are defined as modified polyesters with the addition of fatty acids, which are manufactured from polyhydric alcohols (Polyols) such as glycerol, dicarboxylic acid or carboxylic acid anhydride[1], such as phthalic anhydride, and can also be defined as A type of cross-linked polyester, thermosetting plastic, used by 90% in the form of liquids to paint dishes. It is characterized by its rigidity and dimensional stability even at high temperatures. It is easy to color. It is characterized by transparency, adhesive strength and heat resistance. It is also characterized by being affected by strong acids and bases, and its low resistance to moisture. As pigments for paint and the printing ink industry[2], alkyd resins are by far the most important class of coating resins. It is estimated that alkyd resins contribute about 70% of the traditional binders used in surface coatings today. The popularity of alkyd resins as coating compounds is largely due to They are notable for their unique properties such as

hardness, toughness, and corrosion resistance[3], and can also be defined as products of a polycondensation reaction between acids of various groups. Carboxylic and polyhydric alcohols modified with fatty acids[4], and alkyd resins are one of the most indispensable raw materials in the industries of coatings and paints used for decorative purposes. The reason for their wide use is that their raw materials are cheap and inexpensive, and in addition they are easy to manufacture. The applications of alkyd resins are not only limited to decorative paints, but also in air-curing paints, machine tool coatings, inks, and matte and semi-gloss varnishes for furniture. Wooden and materials that are made to protect the surface from environmental influences[5]. The presence of oil and glycerin as parts of alkyd resins gives them the quality of being environmentally friendly compared to conventional petroleum polymers that pose environmental pollution and degradation. They

have received special attention due to their inherent non-toxic nature and biodegradability[6]. Usually oils or fatty acids used in the manufacture of alkyd resins originate from natural sources such as oil (flax, sunflower, coconut, bitter almond, soybean, castor, palm, cotton) and other natural oils that have long chains for the manufacture of polymeric

resins such as alkyds. Depending on the nature of the unsaturated fatty acids present, the fatty acids included in the composition of the alkyd give flexibility that makes it used in the manufacture of flexible coatings[7]. In this context, we will mention the fatty acid components of some vegetable oils used for coatings in Table (1) below.

Table -1 shows the fatty acid components of some vegetable oils used in coatings[8]

Average number of double bonds for triglycerides	other	Acids saturated	Acid Oleic ^{a)} C18:1	Acid Linoleic ^{a)} C18:2	Acid Linolenic ^{a)} C18:3	oils
3	88 ^{b)}	2	5	4	1	castor
3.6	-	26	19	54	1	cotton
6.6	-	9	19	15	57	linen
1.8	-	51	39	10	-	Palm
4.6	-	16	23	53	8	soybean
-	-	10	42	47	1	sunflower

^{a)}: Number of Carbon: Number of Double bonds

^{b)}: Ricinoleic acid

Experimental Part

The Devices Used

FTIR Infrared Spectroscopy, Electronic thermometer to control the polymerization temperature, Abasin heater equipped with a magnetic stirrer, A sensitive scale for weighing samples, A proton nuclear magnetic resonance (1H NMR) device, Gel permeation chromatography (GPC) for measuring molecular weight, Ostwald capillary viscometer.

Materials Used

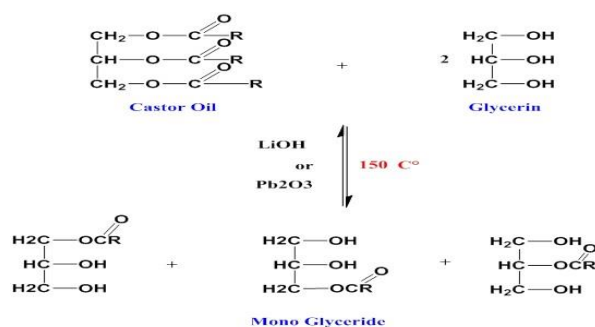
Commercial castor oil from Emad Vegetable Oil Factory Mosul Iraq, Lithium hydroxide (LiOH) from CDH company, Lead oxide (PbO₂) from CDH company, Glycerine from BDH Company, Tartaric Acid (TA) from CDH Company, Calcium Carbonate from CDH Company, Methanol BDH, Sodium Hydroxide (NaOH) from Fluka Company, Nitrogen (N₂) from Iraq.

The Method of Work

The First Step: (The Glycolysis)

In this step, (66 mL) of glycerin is used with 33 mL of commercial castor oil and 0.3 g of lithium hydroxide (LiOH) as a catalyst or 0.3 g of lead oxide (Pb₂O₃), placed in a glass beaker with a volume of (250 mL) and using an engine at a temperature of (150 °C) and for a period of (5 hours) according to scheme (1). Using the separation funnel, the decomposition products are separated into monoglycerides, the bottom of the funnel and the upper part, which forms the unreacted

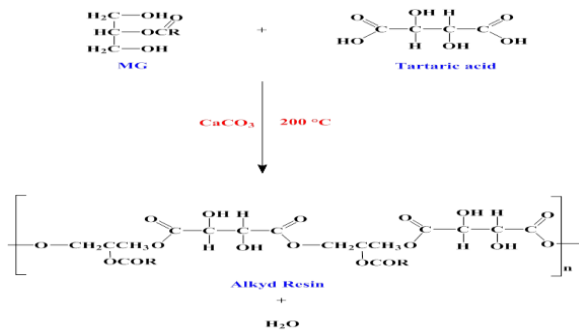
part of the oil, and the bottom part of the funnel, which represents the monomer formed during the polymerization reaction[9].



Scheme-1 Shows Glycolysis

(B) Step Two: (Polymerization)

In this step, the separated bottom part of the monochloride reacts from the separation funnel (monomer), as (50 mL) of the monomer is taken with (20 g) tartaric acid and 0.3 g of catalyst (CaCO₃). It is placed in a glass beaker with Three openings, with different temperatures (170, 180, 190, 200, 210)°C, with a difference of 10 °C for each experiment, and with continuous stirring and using the control unit (electronic thermometer) were connected to the heater, and glass wool resistant to high temperatures was used to maintain the reaction temperature., and the process was completed Polymerization in isolation from oxygen in the presence of nitrogen gas (N₂) (inert atmosphere). The benefit of the inert atmosphere is to prevent the reaction mixture from oxidizing, as well as preventing burning and blackening of the formed polymer, as in the reaction scheme (2) following[10].



Scheme -2 Formation of the polymer in the presence of tartaric acid

3. Results and Discussion

3.1 Polymer Identification

3.1.1 Infrared Spectroscopy (Ftir) Analysis

The prepared polymer was diagnosed using (FTIR) techniques, where it gave absorption bands at frequency (3356 cm⁻¹) due to bonding (O-H) stretching, and two absorption bands for asymmetric stretching at, frequency (2939 cm⁻¹) and for symmetric stretching frequency (2885 cm⁻¹) It belongs to the aliphatic (C-H) bond, and absorption bands at frequency (1743 cm⁻¹) belong to the bond stretch (C=O), and an absorption band at frequency (1643 cm⁻¹) belongs to the bond stretch (C=C) of the alkene in Group (R), and two absorption bands at frequencies (1041 cm⁻¹) and (1273cm⁻¹) belong to the (C-O) group, and an absorption band at frequency (1411 cm⁻¹) belongs to the band (CH2)[11]. As in The following figure(1)

R= Ricinolic acid , the major content of castor oil

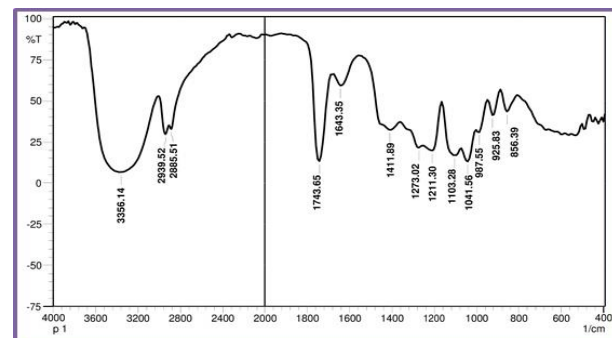
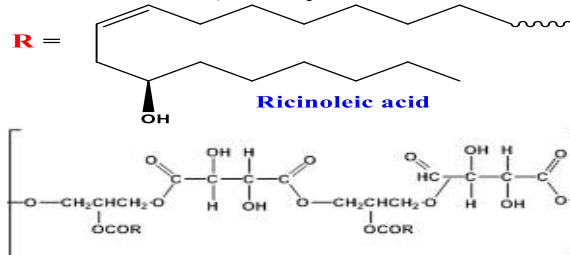


Figure -1 FT-IR spectrum of the polymer prepared from the reaction of (tartaric acid)and

(monoglycerides) in the presence of the catalyst (CaCO₃)

Nuclear Magnetic Proton Analysis (¹hnmr)

The proton nuclear magnetic spectrum(¹Hnmr)of the prepared polymer showed multiple peaks between (1.53-2.32 ppm) belonging to the protons of the (CH3) group present in R, and multiple peaks between (3.10-4.00 ppm) belonging to the protons of the (CH2) group present inR, It also showed peaks at (4.69-5.12 ppm) belonging to the protons of the (CH) group, multiple peaks at (4.00 - 4.69 ppm) belonging to the protons of the (CH2) group, a peak at (5.19 ppm)belonging to the protons of the(CHOH)group, and a peak At (5.66 -5.23ppm) it returns to the proton of the (OH) group in the R group[12] .As shown in the following figure (2):

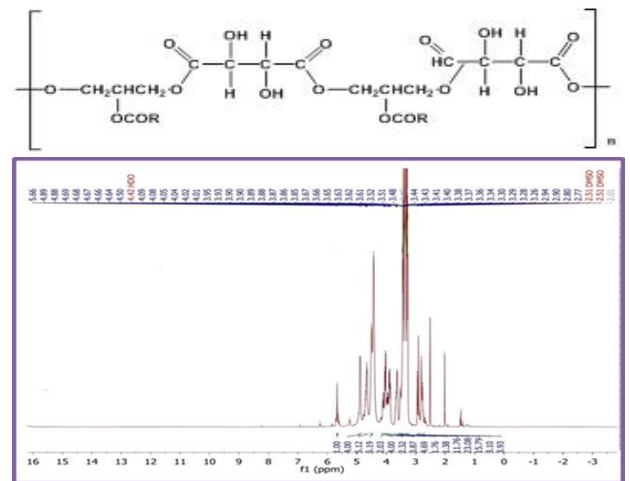


Figure -2 The proton nuclear magnetic spectrum (¹Hnmr) of the polymer measured in DMSO-d₆ solvent.

Reaction Kinetics by Drop Tracin In Acid Value Polymer

The reaction was carried out at different temperatures and at a rate of (20 minutes) between one reading and another of the prepared polymer, and the acid value was calculated from the following equation :

$$1) \dots \left(\frac{V_{NaOH} \times N_{NaOH} \times 40}{\text{Weight of Polymer}} \right) = \text{Acid value}$$

Where: (Acid value) represents the pH value and (V) the volume of NaOH coming out of the burette and, (N) the NaOH concentration (0.01M), (40) represents the molecular weight of (NaOH), and (weigh of polymer) represents (lg) of the weight of the withdrawn polymer During the polymerization process, the kinetics of the polymer P1 was calculated by decreasing the concentration of acid (TA) in the presence of the catalyst (CaCO₃)[13] , as shown in the following figure (3)

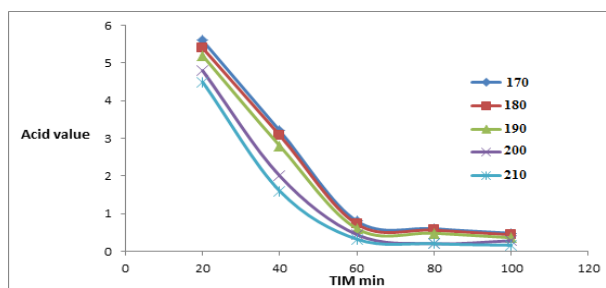


Figure -3 Reaction speed to prepare polymer at temperatures (200, 180, 170, 190, 210) °C in the presence of (CaCO₃).

3.3 Reaction Kinetics By Tracking The Amount Of Water Removed From Polymer

The reaction was carried out at different temperatures and at a rate of 20 minutes between one reading and another, using the catalyst (CaCO₃), as shown in Figure (4).

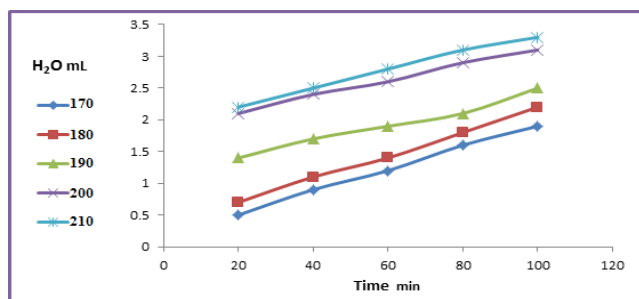


Figure -4 average speed for preparing polymer P1 from the amount of water removed against time at temperatures (170, 180, 190, 200, 210) °C in the presence of (CaCO₃).

3.4 Calculate the Activation Energy

The results were processed using the following Arrhenius equation

$$k = Ae^{-E_a/RT} \dots\dots\dots(2)$$

By taking the natural logarithm (ln) of both sides of the equation, it becomes:

$$\dots\dots\dots(3) \quad \ln k = \ln A - \frac{E_a}{RT}$$

The activation energy was calculated by means of the curves represented in Figures (4), (5), as (k) represents the reaction rate and was obtained by tracking the decrease in acid concentration with time, as well as by tracking the amount of water removed with time, E_a The activation energy is represented in units of (kJ), and a is the frequency factor in units of s⁻¹, and T) represents the absolute temperature in units of Kelvin (K), calculated from the following relationship:

$$T \text{ K} = ^\circ\text{C} + 273 \dots\dots\dots(4)$$

Table -2 represents the relationship between 1/T and lnk for the polymerization reaction depending

on the acid reduction in the presence of the catalyst (CaCO₃) for polymer

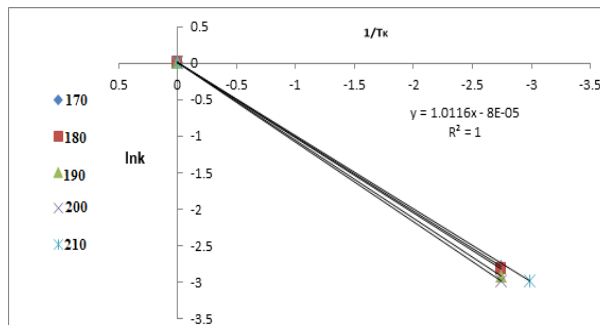


Figure -5 Graphical representation of 1/TK with lnk for the polymerization reaction to prepare polymer depending on a decrease in the acid concentration in the presence of (CaCO₃) and through the use of (NaOH)

And using the Arrhenius equation (3) and the graphic analysis between ln k with 1/T and by means of equation (5) we got the following values:

$$\dots\dots\dots(5) \text{ Slope} = - \frac{E_a}{R}$$

$$8.314 - 1.0116 \times = E_a$$

$$J \text{ k} - 0.00841 = E_a$$

$$\ln A = - 2.739$$

$$A = 0.0646 \text{ s}^{-1}$$

Table -3 represents the relationship between 1/T and lnk for the polymerization reaction depending on the amount of water removed in the presence (CaCO₃) of polymer.

ln k	k	1/T _K	T _K	T (°C)	NO
-4.045	0.0175	0.00226	443	170	1
-3.989	0.0185	0.00221	453	180	2
-4.342	0.013	0.00215	463	190	3
-4.382	0.0125	0.00211	473	200	4
-4.268	0.014	0.00207	483	210	5

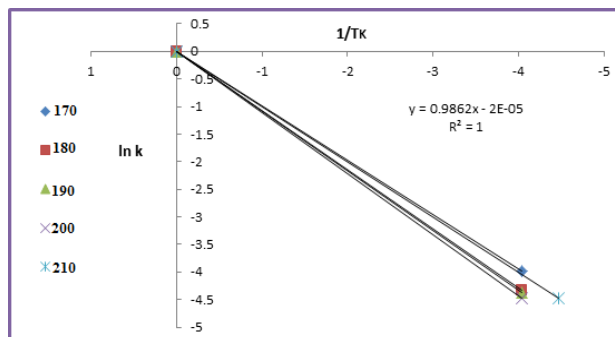


Figure -6 Graph 1/TK with lnk for the polymerization reaction to produce polymer depending on the amount of water removed in the presence of (CaCO₃).

And using the Arrhenius equation (3) and the graphic analysis between ln k with 1/T and by means of equation (5) we got the following values:

$$8.314 - 0.9862 \times = E_a$$

$$J k - 8.1992 = E_a$$

$$\ln A = -4.0391$$

$$A = 0.0176 \text{ s}^{-1}$$

3.5 Calculating Thermodynamic Functions (ΔH° , ΔS° , ΔG°)

The thermodynamic functions of the first P1 polymer were calculated in the presence of the catalyst (CaCO_3) and depending on the decrease in acid value, and using the Vant-Hoff equation for the graph from the calculation of the Erinus equation for Figure (6). The value of (ΔH) is calculated from the slope equation (7), and the value of the entropy change (ΔS) is calculated from

the Intercept equation (8) of the graph when applying the Vant-Hoff equation (6)[14], on the graph in Figure (6):

$$\left(\frac{\Delta S^\circ}{R} + \ln k = \frac{-\Delta H^\circ}{TR} \right) \dots \dots \dots (8) \text{ Intercept}$$

$$\frac{-\Delta H^\circ}{R} \text{ Slope} =$$

Where R is the general constant for gases (8.314 J/mol.K), T is the absolute temperature in Kelvin units (K), and k is the reaction rate constant. The reaction free energy (ΔG) was calculated from Table (2) and the following equation:

$$G^\circ = -RT \ln k \dots \dots \dots (9) \Delta$$

As shown in the following table (4) :

Table -4 showing the functions (ΔH , ΔS , ΔG) for polymer P1 in the presence of (CaCO_3)

ΔS kJ.mol ⁻¹ . K ⁻¹	ΔG kJ.mol ⁻¹	ΔH kJ.mol ⁻¹	TK	T °C
0.00000332-	10.110	0.009-	443	170
	10.458		453	180
	10.828		463	190
	11.463		473	200
	11.994		483	210

Conclusions

In general, it was found that the temperature has a significant effect on the rate of reaction speed for the preparation of the polymer. It is possible to obtain a water-soluble polymer, which has an economic, positive and environmental impact to reduce the use of organic solvents. We found that the catalyst has a great effect on the speed of polymerization reactions, and this factor is CaCO_3 . It is possible to rely on the decrease in the acid value and the amount of water removed from the polymerization process to study its kinetics. Other non-traditional methods such as (GPC) can be adopted to determine the molecular weight because they need more research and comparison.

Conflicts Of Interest

The authors make it clear that they do not have any Conflicts of interest in this work.

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