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Synthesis and characterization of new styrenated alkyd Resins derived from olive oil based by polyester resin modified with maleic anhydride and phthalic anhydride

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Abstract

Three alkyd resins from olive oil were prepared using phthalic anhydride, maleic anhydride, and glycerol at stipulated ratios. The various physic-chemical properties of alkyd resins including acid value, saponification value, iodine value, Density, viscosity, chemical resistance and volatile matter were studied. The result is that alkyd resins are readily soluble in aprotic polar solvents such as (Toluene, Acetone, Benzene, xylene, DMF, DMSO, Methanol, and ethanol) without being in need for heating. The prepared alkyd resins were copolymerized with styrene using benzoyl peroxide (BPO) as the free radical generator at 150°C for 3 h. The styrenated alkyds and palm kernel oil-modified alkyds were all characterized for their physical-chemical properties following standard methods. The styrenated and unstyrenated alkyds were tested for drying schedule, solubility, adhesion, abrasion resistance and chemical resistance. All the resins showed good properties. The styrenated alkyds gave faster drying time, and chemical resistance. Unlike the unstyrenated alkyd which was only resistant to water, brine, and acidic media, the styrenated alkyds were also resistant to alkalis. Thermal analysis of styrenated and alkyd resins is conducted by using thermo Gravimetric Analysis (TGA) and thermal differential calorimeter (DSC) techniques, which reveals that these aromatic styrenated alkyd resins possess thermal stability. Styrenated and alkyd resins were characterized by FTIR and ^{1}HNMR spectroscopies. It can be concluded that styrenated alkyds offer improved potential applications in surface coating purposes.

Key words: Styrenated alkyd resins, Olive oil, Alkyd resins, Chemical resistance, Maleic anhydride and Phthalic anhydride, Acid value

INTRODUCTION

Alkyd resin or oil-modified polyester, traditionally, is the most extensively used synthetic resin in the surface-coating industry. Alkyd-based coating is well known for its fast dryness, good corrosion protection, high gloss and ease of application even over poorly treated surface. The chemistry of the structural units connecting the ester groups allows alkyds to have immense diversity and versatility, such as labile biomedical matrices, liquid crystals, fibers and temperature resistant performance materials [1-4].The demand for alkyd resin for use in the surface coating industry has been increased tremendously in recent times [5]. Consequently, there is an increased demand for drying oils required for the production of alkyd resins. These drying oils, which are regarded as standards in surface coating industry are still very scarce and expensive. Moreover, their alkyds are prone to yellowing due to high unsaturation. Preliminary investigations have revealed the potential sources that could meet the country's requirement of vegetable oil for alkyd production when properly developed [6-7], and olive oil is one of them. Olive oil has become one of the major edible oils in the world. It is classified as non-drying oil because of its low iodine value; olive oil alkyds are not capable of forming coherent film by air oxidation. The limited unsaturation in the fatty acid chains of this oil is responsible for its inferior curing properties compared to other drying oil based resins. Thus, curing agent and dryer are needed in the curing process. There is little or no report on the use of olive oil alone in making alkyds for coating application. Despite the advantages of olive oil-modified alkyds such as good adhesion, film flexibility, color, gloss broader temperature range application, etc., there are some drawbacks, for instance, its susceptibility to alkali as a result of splitting of the ester linkages by hydrolysis; this reaction is very typical of esters. In addition, compared to other synthetic resins, olive oil-modified alkyd resin is relatively slow in drying. However, it has been demonstrated that nondrying oil can be modified by several physical (blending) and chemical (copolymerization) processes to give products that could meet up with a wide range of applications. The present study, therefore, seeks to investigate the effect of styrene modification on the properties of olive oil alkyd resin as it is known that polystyrene is very resistant to the action of alkali both in alcoholic and non-aqueous media.

MATERIALS AND INSTRUMENTS

Materials

Olive oil, Pentaerythritol, glycerol, Methanol, Acetone, Toluene benzene and Carbon tetrachloride from (BDH- Chemicals Limited Poole/ England) Phthalic anhydride , Lead oxide, Lead oxide , Xylene ,Tetra hydro furan(THF),propylene glycol ,Malic anhydride and Dimethyl Sulfoxide(DMSO) from (MERCK – Schumann /Germany). Phenolphthalein, Carbon tetrachloride, ethanol ether (Scarab S.L./Spain).Hydrochloric acid , Sodium chloride, Potassium hydroxide, Potassium Iodide, Sodium thiosulfate from (HIMEDIA Hi Media/India). Sulfuric acid from (SD fine- CHEM Limited / India). Di methyl form amide from (Scarab S.L./Spain). Hydroxide (Water purification company Baghdad). Styrene (Aso-San / Turkey).

Instruments:

FTIR Spectrophotometer Infrared spectra were recorded in the Department of Chemistry at College of Engineering at the University of Al-Qadisiyah with a device from (Shimadzu) of the type (8400).The Balance A sensitive balance with four levels after zero of Sartorius / BL2105Germany was used. Thermogravimetric analysis (TGA) Measurement was done using Polymer laboratories co. England, Model PT-1000 in the central laboratory / College of Pure Sciences - University of Tehran, with a heating rate of 10 m / min under a helium cover, and a temperature of (25-300) nuclear magnetic resonance spectrum (^{1}H-NMR) It was recorded using a Bruker, Ultra Shield 500 MHz spectrometer (Swiss origin) using (DMSO-d6) as a solvent. And at the University of (Education Education) Tehran - Iran. Differential calorimetric thermal analysis (DSC) The measurement was made using a differential thermal analysis device (DSC) type (DSC 131 Eva, SETARAM) of (France) origin and at the University of Tehran / College of Pure Sciences / Department of Chemistry. Oven drying oven type Hot Air Sterilizer Laboratory Oven / M6040P / Germany was used. The Headmen: A thermal heater was used for heating with a temperature of more than 250 ^{c}o. of the type Jenkins / HV65 / England. The Viscometer: A viscometer was used to measure the viscosity of alkyd resin samples prepared in the Department of Chemistry / College of Education / University of Al-Qadisiyah / by a device from (Brookfield) company of type (RVDV- II + P 8500) with a voltage (230

V ~) and a frequency (50/60 Hz).) and with a power of (30 VA). The device was manufactured in (U.S.A).

Preparation of alkyd resin from olive oil:

Several alkyds resins were prepared by using dehydrated Olive oil in presence of glycerol, Pentaerythritol, and propylene glycol with phthalic anhydride, and maleic anhydride using lead (ii) oxide as catalyst using the formulations. The reactions were carried out in a three necked round bottom flask titled with a motorized stirrer, a dean-stark trap titled with water-cooled condenser and nitrogen in let tube at a temperature of 230-2500C. Xylene was also employed as the zeotropic solvent. Two stages were involved State 1 (Alcoholics): At this stage, the measured quantity of dehydrated palm kernel oil was poured into the flask and heated to about 120^{0}C to remove moisture. The heating was achieved with a heating mantle. Thereafter, the measured quantity of glycerol was added and the temperature was raised to 230^{o}C. After 30 minutes, a small quantity of the aliquot was taken to check for its solubility in methanol. The reaction mixtures was cooled to about 140^{o}C. In Stage 2 (Esterification process): At this stage, the measured quantity of phthalic anhydride, maleic anhydride and xylene was added into the flask and heated with a heating mantle. The temperature was gradually raised to about 2300C and maintained at a range of about $230\text{-}250^{0}$C for about 3hours. Aliquots were withdrawn from the reaction mixture at time intervals of 30minutes to check for drop in acid value. The reaction was then discontinued as soon as the acid value of the mixture attained the value of about 10mg K0H/g.

Table (1) Recipe of the preparation of resins

Raw materials	Weight (g)	Weight (%)
olive oil	25	12.047
Phthalic anhydride	12.5	6.023
Maleic anhydride	12.5	6.023
Alcohol	50	4.911
Catalyst (Bo)	0.5	0.25
Total	100.5	29.254

Preparation of styrene alkyd resin:

The styrene alkyds were prepared by post co-polymerization of the alkyd resin. The alkyds were with-draw into 100ml flask in the presence of an initiator, benzoyl peroxide (0.605 gm). The mixture was stirred and heated under reflux at 120^{o}C for 3hrs in the presence of nitrogen. The polymer was thinned with xylene and applied as thin films on glass panel and air dried without the aid of a drier.

Table (2). Recipe of the preparation of styrenated alkyd resins

Alkyd	Styrene
10 (gm)	3 (gm)
10 (gm)	4 (gm)
10 (gm)	5 (gm)

Chemical properties alkyd resin

Acid number

Acid value was determined according AOAC method and to standard 969.17 1997

Iodine number

Deliver (0.1) g sample to (300) ml conical flask with ground in stopper. Add 20 ml carbon tetrachloride and seal. Dissolve Sample in an ultrasonic washing machine, then add 25 ml Hans solution, and seal. Shake for one minute, then keep it sealed and leave in a dark room (about 20 "C) for 30 minutes. Then add (10) ml of 15% potassium iodide and 100 ml water, and seal. Shake for (30) seconds, then titrate with (0.1)mole / L sodium thiosulfate to obtain iodine value then also perform blank test to obtain blank level.

Saponification Number

Weight (I gm) of sample into an Erlenmeyer flask, in pipette 25 ml of 0.5N KOH put in the flask, then add 4 ml of the solvent (ethanol-ether) to the flask, then reflux for (30) minutes, rinse the inside of the condensers with about (25) ml DI water allow the solvent to drain into the Erlenmeyer Mask, and allow the solution to cool to room temperature, then add three to five drops of phenolphthalein indicator to the solution with moderate agitation, then add (0.5) HCI (titrant) to the burette, and not level, then add titrant from the burette to the solution until the faint pink color permanently (for at least thirty seconds) disappears, and not level of titrant in the burette.

Physical properties of alkyd resin

Density

The density was determined according to NF EN 1097-6 using analytical scale and pycnometer S9611826 (100 ccs).

Drying

Aluminum plates were cleaned by ethanol to make sure that there are no contaminants present to affect the result. A land coater with different fixed thickness was used to evenly coat the resin on the surface of the testing plates.

Viscosity

Brookfield rotary Viscometer Ku-2 model RVDV-II P8500 was used to measure the viscosity at 25 °C; and using different spindle and speed.

Volatility

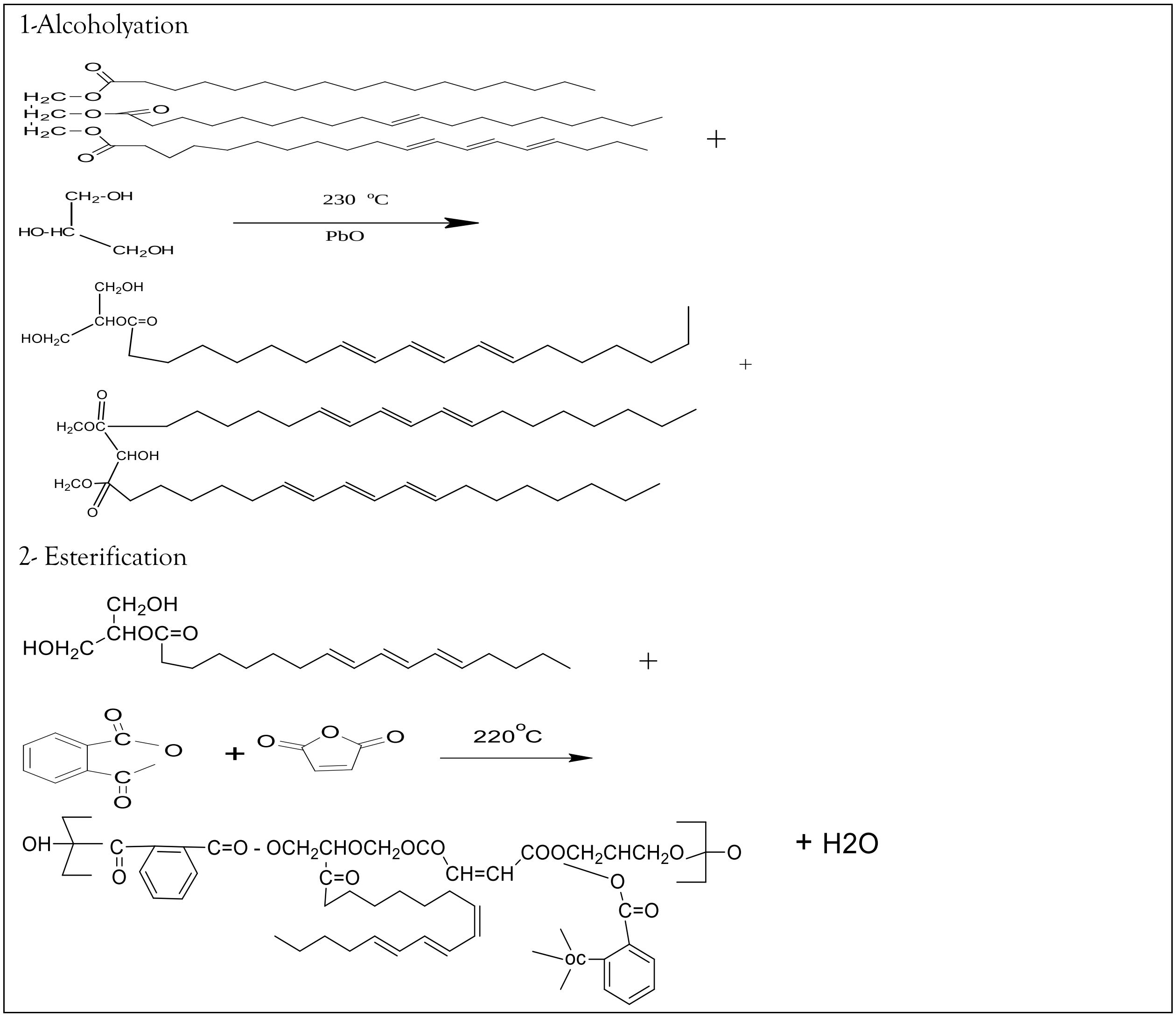
Three specimens were placed in the oven within (30) min after preparation of alkyd resin in previously weighed watch glass and heated for (2 h) at (135-140)^{o}C. The Nonvolatile matter was calculated from the difference in initial and final weights of the watch glass. The mean value of the three results was reported as the percentage nonvolatile matter.

Results and Discussion

Synthesis and Characterization of alkyd resin

Synthesis and characterization of alkyd resin from Olive oil with glycerol (O-G)

This alkyd resin was synthesized by the condensation of Olive oil with glycerol and phthalic anhydride and malic anhydride in the presence of lead oxide as catalyst at temperature (120-240 ^{o}C) for (6 hours) in the presence of N_2 according to the scheme (1):



Scheme (1) Synthesis of alkyd resin from Olive oil with glycerol

FTIR spectrum of alkyd resin from Olive oil with glycerol (O-G)

The FTIR spectrum of (OG) which indicates the appearance of absorption band at (3550 cm for (OH) of Carboxylic acid. While the emergence of two distinct bands at the two frequencies (2854, 2923Cm^{-1}) is due to the vibration of the stretching of the aliphatic (C-H) bond, also the appearance of the peak at the frequency (1765Cm^{-1}) is due to the vibration of the stretching of the bond (C=O) in the ester group. Also, the appearance of the peak at frequency (1465 Cm^{-1}) is due to the vibration of the aromatic bond (C=C), and the appearance of the peak at frequency (1615 Cm^{-1}) is due to the vibration of the bond stretching (C=C) of the alkene, as well as the appearance of the peak at frequency (1110 cm^{-1}) to the (C-O) straining vibration [8-9-10]

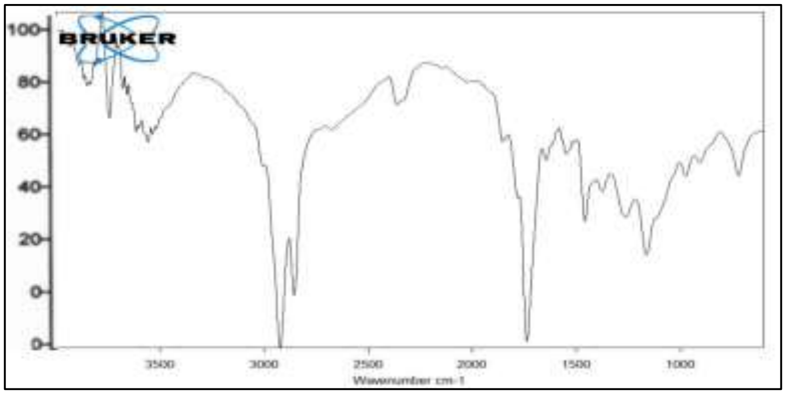


Figure (1) FTIR spectrum of alkyd resin from olive oil with glycerol

^{1}HNMR spectrum of alkyd resin from Olive oil with glycerol (O-G) ^{1}HNMR Spectrum of (OG) assigns the following chemical shifts. (δ = 0.7 ppm) for methyl group, (δ = 0.7 ppm) for (CH2), (δ= 4.6 ppm) for (OCH_2), singles (δ = 6.2-7.1 ppm) for Ar-H group, (δ= 13.3 ppm) for COO [8-9-10].

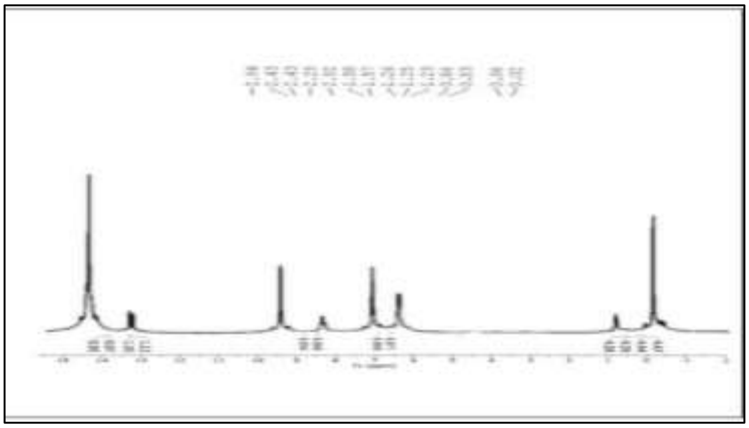
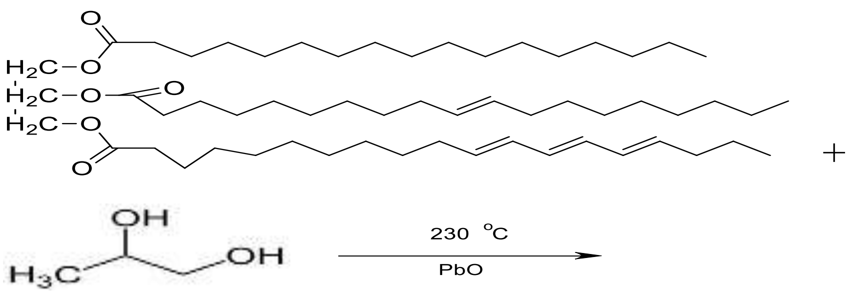


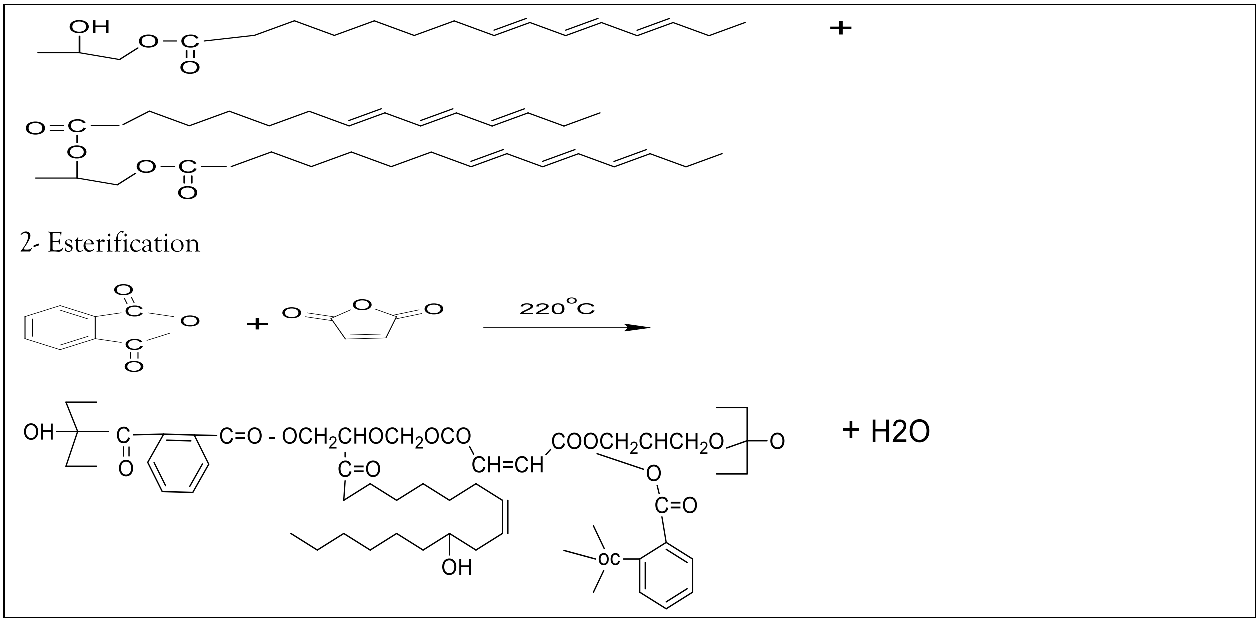
Figure (2) ^{1}HNMR spectrum of alkyd resin from olive oil with glycerol

Synthesis and characterization of alkyd resin from Olive oil with propylene glycol (O-PR)

This alkyd resin was synthesized by the condensation of Olive oil with propylene glycol and phthalic anhydride and malic anhydride in the presence of lead oxide as catalyst at temperature (120-240 °C) for (6 hours) in the presence of N_2 according to the scheme (2):

1-Alcoholyation





Scheme (2) Synthesis alkyd resin from Olive oil with propylene glycol

FTIR spectrum of alkyd resin from Olive oil with propylene glycol (O-PR)

The FTIR spectrum of (OPR) indicates the appearance of absorption band at (3550 cm for (OH) of Carboxylic acid. While the emergence of two distinct bands at the two frequencies (2854, 2923Cm^{-1}) is due to the vibration of the stretching of the aliphatic (C-H) bond, also the appearance of the peak at the frequency (1765Cm^{-1}) is due to the vibration of the stretching of the bond (C=O) in the ester group. Also, the appearance of the peak at frequency (1465 Cm^{-1}) is due to the vibration of the aromatic bond (C=C), and the appearance of the peak at frequency (1615 Cm^{-1}) is due to the vibration of the bond stretching (C=C) of the alkene, as well as the appearance of the peak at frequency (1110 cm^{-1}) to the (C-O) straining vibration [8-9-10].

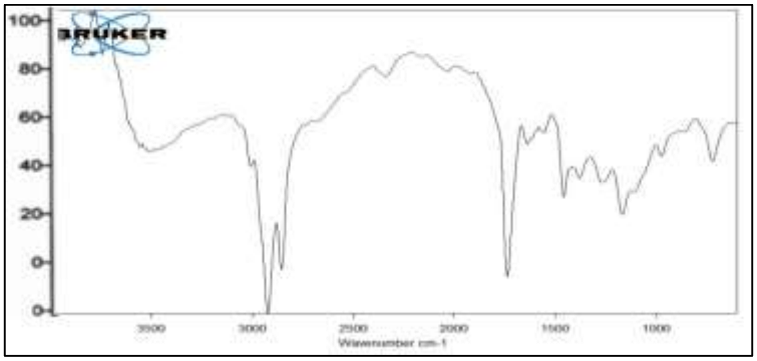
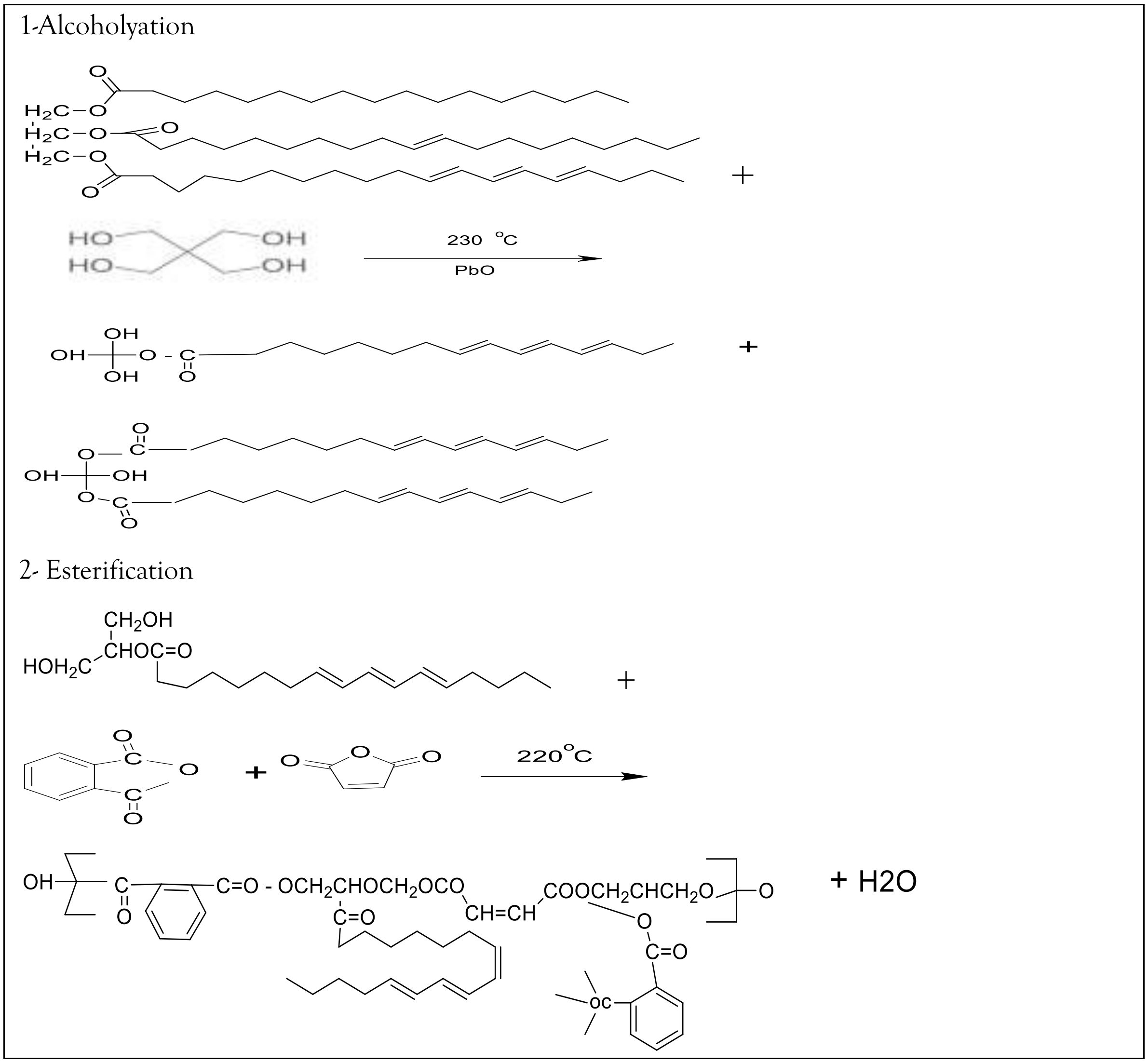


Figure (3) FTIR spectrum of alkyd resin olive oil with propylene glycol

Synthesis and characterization of alkyd resin from Olive oil with Pentaerythritol (O-PE)

This alkyd resin was synthesized by the condensation of Olive oil with Pentaerythritol and phthalic anhydride and malic anhydride in the presence of lead oxide as catalyst and temperature at (120-240 ^{o}C) for (6 hours) in the presence of N_2 according to the scheme (3):



Scheme (3) Synthesis of alkyd resin from Olive oil with Pentaerythritol

FTIR spectrum of alkyd resin from Olive oil with (Pentaerythritol (O-PE)

The FTIR spectrum of (OPE) which indicatesThe appearance of absorption band at (3550 cm for (OH) of Carboxylic acid. While the emergence of two distinct bands at the two frequencies (2854, 2923Cm^{-1}) is due to the vibration of the stretching of the aliphatic (C-H) bond, also the appearance of the peak at the frequency (1765Cm^{-1}) is due to the vibration of the stretching of the bond (C=O) in the ester group. Also, the appearance of the peak at frequency (1465 Cm^{-1}) is due to the vibration of the aromatic bond (C=C), and the appearance of the peak at frequency (1615 Cm^{-1}) is due to the vibration of the bond stretching (C=C) of the alkene, as well as the appearance of the peak at frequency (1110 cm^{-1}) to the (C-O) straining vibration [8-9-10].

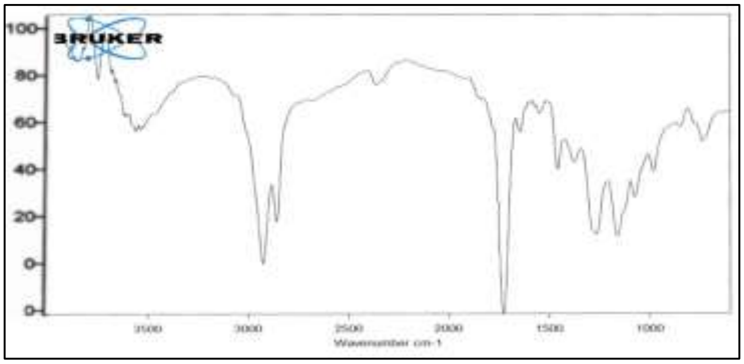


Figure (4) FTIR spectrum of alkyd resin from olive oil with Pentaerythritol

^{1}HNMR spectrum of alkyd resin from Olive oil with Pentaerythritol (O-PE)

^{1}HNMR spectrum of (OPE) assigns the following chemical shifts. (δ = 0.7 ppm) for methyl group, (δ = 1.5 ppm) for (CH2), (δ= 3.4 ppm) for (OCH_2), single (δ = 7.1 ppm) for Ar-H group. (δ= 2.5 ppm) for (DMSO) [8-9-10].

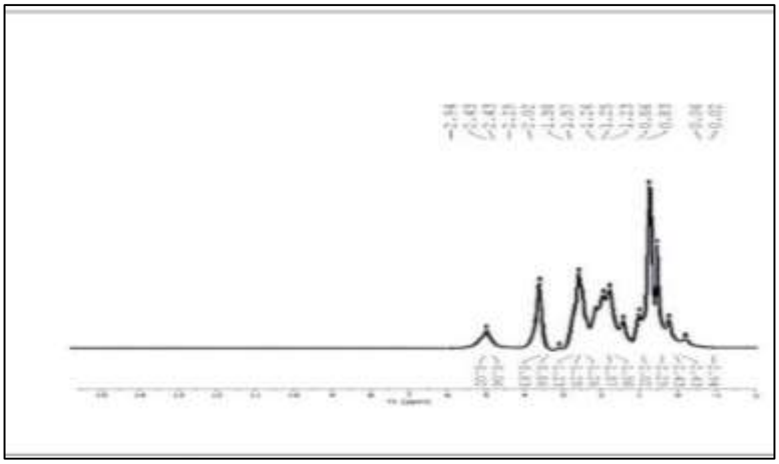


Figure (5) ^{1}HNMR spectrum of olive oil with Pentaerythritol

Chemical properties of alkyd resin

Acid value : It is useful to determine the acid value to find out the number of milligrams of potassium hydroxide KOH needed to neutralize one gram of the model (the prepared resin), and it is measured by the amount of carboxylic acid groups in chemical compounds such as fatty acids.

An increase in this value is an indication of the occurrence of rancidity of the fatty substance, as there is an allowable limit for the amount of free fatty acids present in the triglycerides (oil). This characteristic is important in evaluating the quality of oil seeds at the time of extraction. These seeds contain an enzyme (lipase), which decomposes under suitable conditions of humidity and temperature into triglycerides (oils). Therefore, a good storage process for these seeds is very important in preventing oil seeds from spoiling and reduces the production of fatty acids in oil seeds. When manufacturing resins Alkyd free fatty acids are rapidly inactivated in alcoholic reactions, so damaged vegetable oil is not suitable for the manufacture of alkyd resins [11].

This test was applied to all alkyd resin prepared by taking 0.2 gm of it and putting it in 5 ml of methanol and then rinsing it with potassium hydroxide solution using phenolphthalein as an index to obtain the neutral point when the color changed.

It was noted from the results shown in Table (3) that changes occurred between each resin prepared according to the type of oil used and its storage period. The acid value of the prepared resin increases with the increase in the length of the fatty acid chain of which the vegetable oil is composed. The alkyd resins prepared from olive oil has (17) carbon atoms, therefore The olive oil showed the lowest acid value, due to the short chain of fatty acid .

Table (3) shows the acid values of the prepared alkyd resins

Alkyd resins	Acid value (mg KOH g^{-1})
O-G	9.3
O-PR	9.2
O-PE	**9.5**

Iodine number

It is the number of grams of iodine needed to saturate the double bonds present in 100 grams of fat. It is a property that can be used to measure the degree of unsaturation (double bonds) in unsaturated fatty acids (note that the iodine number of saturated fatty acids = zero). The iodine number is also used to detect adulteration of vegetable oils, as it is considered one of the constants of oils. If the iodine number is high, it means that it contains a high percentage of unsaturated fatty acids. If the iodine number is low, it indicates the saturation of the fatty acids [12].

The results were noted for the alkyd resins prepared through Table (4). Olive oil contain double bonds in their composition, and as was said previously, the iodine number measures the degree of unsaturation (double bonds). While it is noted from the results that alkyd resins from olive showed the lowest value of iodine number because the short chain of olive oil (C17) and the presence of unsaturation in small quantities in the chain.

Table (4) shows the iodine number values for the prepared alkyd resins

Alkyd resins	Iodine number (gI_2/100 g)
O-G	120
O-PR	119
O-PE	**121**

Saponification number

It is the number of milligrams of potassium hydroxide needed to spoon (1 gram) of fat or oil. The saponification number (value) is used:

A) Know the length of the fatty acid chain in glycerides, as the value of saponification is inversely proportional to the length of the fatty acid chain (the lower the saponification value, the longer chain fatty acid and vice versa) because it has the lowest relative number of functional (effective) carboxyl groups per unit mass of fat Balancing with short chain fatty acids.

b) Estimating the approximate molecular weight of the fat (particularly mixed poly glycerides), also, and the saponification number is one of the important constants for the identification of some oils [13].

The results were observed from Table (5), the saponification number is inversely proportional to the length of the fatty acid chain, as well as having relatively fewer carboxyl functional groups (active) in balance with the short chain of fatty acids, therefore the saponification value of alkyd resins from olive oil are high.

Table (5) shows the saponification values of the prepared alkyd resins

Alkyd resins	Saponification Number (mg KOH g^{-1})
O-G	233
O-PR	230
O-PE	240

Physical properties of alkyd resin

Density

The density of the prepared alkyd resins was determined according to the standard NF EN 1097-6 (using a Pycnometer according to specification S96118226). The test was applied by taking a quantity of the prepared resin and placing it in the Pycnometer and calculating the weight of the resin with the Pycnometer and then finding the difference in weight between the Pycnometer when it was filled and when it was empty according to the volume Pycnometer (25 ml).

The results were observed for the resins prepared in Table (6), the density of alkyd resins decreased with the increase in the length of the fatty acid chain and vice versa, also, due to the presence of the lowest relative number of active carboxyl groups. It is noted that the alkyd resins prepared from olive oil showed a high density than the alkyd due to the length of the fatty acid chain of which the oils are composed, which is inversely proportional to the density of alkyd resin.

Table (6) shows the density values for the prepared alkyd resins

Alkyd resins	**Density (gm/Cm^3)**
O-G	0.97
O-PR	0.98
O-PE	0.95

Drying time

The unsaturation in the fatty acid chains is unaffected during alkyd resin manufacture and so the mechanism of film formation in such alkyds is same as that of oils. The molecular weight of alkyds is higher than that of oil so less cross-link are required to form a film resulting in rapid drying as compare to corresponding oil.

Semi-drying oils discolor less on drying than the highly conjugated drying oils. Keeping the above point in mind, resin formulator can employ semi-drying oils in alkyds to have rapid drying capability with better color. Oil lengths of 50-60% are generally used for such alkyds but it must be remembered that though higher oil length provide improved drying rates, they also adversely affect color and gloss retention as well as durability of film. There are two types of drying: physical drying, and chemical drying. Chemically dried are alkyd resins. These resins are characterized by the fact that they dry quickly due to the fact that most of the fatty acid chains included in the composition of these oils are unsaturated, which makes them have the ability to interact with air oxygen, that is, the drying process occurs as a result of the occurrence of the oxidation and polymerization process of the alkyd resin, and the auto-oxidation mechanism is a complex process [11] And there are more than one type of intermediates that can be formed, and the double bonds in fatty acids or vegetable oils may be conjugated or unconjugated, and the form of the double bonds has effects in drawing cross-linking [11,12], which is formed in the polymerization process, and in general, the auto-oxidation process is divided into five [12] stages They are 1) initiation, 2) hydro peroxide formation, 3) hydro peroxide dissociation, 4) crosslinking, and 5) dissolution. It was noted through the results shown in Table (7) the difference in the drying time between each prepared alkyd resin depending on: a) the length of the fatty acid chain of which the alkyd resin is composed, so the drying time of alkyd resins prepared from olive oil is less dry due to the location of the double bonds on which the drying process (oxidation) takes place, and the number of daily carbon atoms is of particular importance because it distinguishes the centers transverse entanglement.

It also depends on the type of vegetable oil used. Among the best oils used in the production of dried resins are (Olive oil) by removing water from it .The thickness of the aluminum plate on which the model is placed. If the thickness of the plate is 120 µm, it requires more time to dry. Balance with the aluminum plate, whose thickness is 30 µm. The dried used (solvent) in order to speed up the drying process because without the drier the process would be very slow but the amounts of driers should be kept to the lowest possible level because they not only stimulate drying but also stimulate the reaction after drying which causes brittleness, splitting and color change.

Table (7) shows the drying time values for the prepared resins

Alkyd resins	**Drying Time (min.)**
O-G	45
O-PR	56
O-PE	30

Viscosity

The viscosity of the solution is an important method for the characterization of polymers, as it is a measure of the molecular weight of the polymer, as the viscosity of the solution is a measure of the volume, and the polymer solutions are distinguished by a unique characteristic from the solutions of other materials by being more viscous. Among the factors affecting viscosity:

A) Pressure: The effect of pressure on viscosity is of little importance, but the effect of viscosity appears when the pressure exceeds (68 bar).

B) Temperature: When the temperature increases, the viscosity of liquids decreases; when the temperature of the liquid increases, the distances between the molecules increase, so the friction between them decreases, and then the viscosity decreases [13]. It is noted that the viscosity of alkyd resins increases during the reaction for all types of oils used in manufacturing. It is also noted that the viscosity increases slowly during the hours (2-3) of the reaction. After that, the viscosity increases significantly in the esterification reaction between mono glycerides and phthalic anhydride and maleic anhydride. After 5 or 6 hours the reaction ends and the alkyd resin is very viscous, i.e.: the polymeric chains are in the form of a gelatinous substance.

According to this test, using a viscometer (RVDV-II + P 8500), with a voltage of (230 V˜), a frequency of (50/60), and a power of (30) VA.

It was noted through the results shown in Table (8) that the viscosity of alkyd resins differs according to the vegetable oils they are composed of. It is noted that the viscosity is high for short-chain resins prepared from olive oil , and the viscosity value decreases in long-chain fatty acid resins. due to the presence of the double bonds associated in the chains of fatty acids.

Table (8) shows the viscosity values of the prepared alkyd resin resins

Alkyd resins	**Viscosity (CP)**	**Temperature**	**Number of spindle**	**Speed of viscosity**
O-G	1776	25	63	60
O-PR	1420	25	63	60
O-PE	**High Viscosity**	**25**	**63**	**60**

Volatility

This test was applied by taking an amount of alkyd resin samples prepared about (0.2 gm) and placing them in a dish glass and weighing them, then inserting them into the oven at a temperature of (140 ° C) for two hours, and then calculating the difference by weight before and after entering the oven. The results of the volatility value of the prepared alkyd resins were noted in Table (9), as it shows the difference in the volatility value between each prepared resin, so the alkyd resins from olive oil show the lowest volatility value due to the short chain of fatty acid consisting of olive oil . While the alkyd resins showed a high volatility value due to the long chain , which contains double bonds with the ability to interact with oxygen, so it volatilizes quickly.

Table (9) shows the volatility values of the prepared alkyd resins

Alkyd resins	Volatile percent (%)
O-G	65
O-PR	63
O-PE	**67**

Chemical resistance

The resistance of the prepared alkyd resins to some chemicals was tested; As it was noted from the results shown in Table (10) the difference in chemical resistance between each resin; As it is noted that the resins prepared from olive oil are resistant, i.e. (insoluble) in water, because the resins are a component from a series of unsaturated fatty acids, that is, they are non-polar organic compounds, and water is a polar solvent. Also, all previous resins are resistant in a Tetrahydrofuran (THF) solvent, because it is a non-polar organic solvent. It is also noted that the resins prepared from olive oil are resistant in hydrochloric acid, sulfuric acid, sodium hydroxide and sodium chloride. While these resins are non- resistant (soluble) in the KOH, and the reason is due to the different type of vegetable oils from which alkyd resins are made according to their nature and the extent of their resistance to solvents.

Table (10) shows the chemical resistance values of the prepared alkyd resins

Alkyd Resin	Dist.H_2O	HCL	H_2SO_4	KOH	NaCl	THF
O + G	+	+	+	-	+	+
O + PR	+	+	+	-	+	+
O + PE	**+**	**+**	**+**	**-**	**+**	**+**

(_) denotes non-resistant alkyd resins (melted)

(+) denotes the insoluble resistant alkyd resin

Solubility

The solubility of alkyd resins was conducted qualitatively in some common organic solvents and is summarized in Table (11). The solubility was measured by taking (0.01 g) of the prepared resin sample and dissolving it in (2 ml) of solvent. Polar aprotic solvents of these solvents (DMF, Acetone, Toluene, Xylene,) and non-polar solvents such as (Benzene, $CHCl_3$) and other solvents such as methanol, ethanol and kerosene. It increases the rate of reaction rate, i.e. the rate of formation of polyester. This is due to the hydrogen bonding between the oxygen atom of the carboxyl ester group (O- Carboxyl ester) and the solvent. In addition, the (acid-base) interaction between the solvent and the polyester (alkyd resin) prevents proton dissociation.

Also among the factors affecting solubility (temperature, stirring and surface area), it is noted, also, through Table (11) that resins prepared from olive oil are dissolved in these solvents , and the solvents molecules attack the chain and dissolve these resins easily.

Table (11) shows the solubility of alkyd resins

resin	solvent							
	Xylene	DMF	Toluene	Acetone	DMSO	Benzene	Methanol	Ethanol
O + G	+	+	+	+	+	+	+	+
O + PR	+	+	+	+	+	+	+	+
O + PE	+	+	+	+	+	+	+	+

+ Soluble at room temperature

Thermal Gravimetric Analysis (TGA) Study for the prepared alkyd resins:

Thermal stability is defined as the specific temperature at which the chemical decomposition of polymers begins, accompanied by volatile products, or it is the maximum temperature to which the polymer is exposed without noticeable changes in an atmosphere of nitrogen, oxygen, or an inert gas [14]. Thermal stability is one of the most important thermal properties, through which it is possible to know the possibility of using polymers in applied fields in which the material is exposed to high temperatures. Several techniques were used to study the thermal stability of polymers, including thermal gravimetric analysis (TGA), which is one of the techniques used to evaluate and study the thermal stability and flame rear Dancy of the polymeric materials under study [15]; this is done by determining the change in weight that occurs when the sample is heated. The chemical changes that occur during the heating process from the sample's loss of weight indicate the occurrence of a process of disintegration (shattering) of the materials subject to measurement [16]. The weight loss caused by the disintegration of materials forms a curve (TGA) and this curve provides useful data and information regarding the properties of the material being measured. The thermal behavior of the polymers prepared through this technique (TGA) has been determined, in an atmosphere of inert Nitrogen gas, with a heating rate of (10°C per minute) and a temperature of (25-300 °C), so the (TGA) technique can serve as a useful indicator. To know the decomposition of polymeric materials, and this method is the most preferable to know the evaluation, balancing and arrangement of thermal stability of the polymers under study. It is observed that the initial weight loss process It for alkyd resins. It started slightly from (130°C) to (200°C). Then, the process of losing weight by increasing up to (600 °C), the increase in weight loss could be due to chemical reactions with gaseous substances that lead to the formation of non-volatile compounds or due to the physical transformation that occurs due to the absorption of gaseous substances by the alkyd resin [17] ; It was also noted that the temperatures when alkyd resins lost 50% of their weight (T50%) increased from 500 to 750 °C, while the percentage of the residue was at 800 °C for alkyd resins ranged between (40-55%), as the high carbonization rate of the prepared alkyd resins was at 700 °C (Char%) Ranging between (62-98%), some high rates of carbonization act as an insulating layer or as a barrier that reduces the decomposition of the lower layers of alkyd resins and thus increases thermal stability and combustion resistance. Also, the increase in aromatic compounds in the alkyd resins composition increases the charring rate, and this makes its decomposition more difficult. Also, the presence of (methylene, hydroxyl) groups in its composition increases stability [18].

Table (12): Thermal behavior data of alkyd resins

Samples	TGA (°C)					Residue % at 800 Ċ	Chart % at 700 Ċ
	T_i	T_{op1}	T_{op2}	T_f	$T_{50\%}$		
O + G	200	350	500	800	500	40	62
O + PE	130	550	710	800	700	50	67
O + PR	200	400	700	800	750	55	98

Ti: Initial decomposition temperature.

Top: Optimum decomposition temperature.

Tf: Final decomposition temperature. The final degree of dissociation temperature

T50%: Temperature of 50% weight loss, obtained from TGA.

Char% at 700 ° C.

Residual weight percentage at **800** ° C.

Differential Scanning Calorimeter Analysis (DSC) Study for the prepared alkyd resins:

This type of analysis expresses the amount of energy absorbed from the sample during its heating and cooling or at a constant temperature. And the degree of crystallization (Tc) [18].

Figure (7) for a sample prepared from the interaction of olive oil with glycerol shows, and the results showed the glass transition value (Tg) of the mixture (150°C), indicating an increase in the temperature flow, and then the sample absorption rate increased. For heat until it reaches the melting point (Tm) at (450^{o}C).

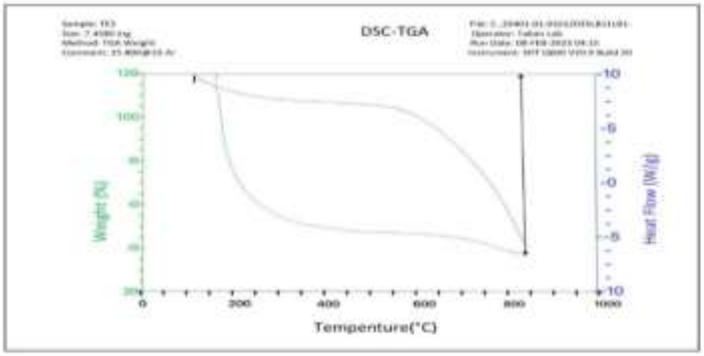
figure (6) for a sample prepared from the interaction of olive oil with propylene glycol shows, and the results showed the glass transition value (Tg) of the mixture (100°C), indicating an increase in the temperature flow, and then the rate of heat absorption of the sample increased to The melting point (Tm) reaches (430°C) .

figure (8) for a sample prepared from the interaction of olive oil with Pentaerythritol shows, and the results showed the glass transition value (Tg) of the mixture (170°C), indicating an increase in the temperature flow, and then the rate of heat absorption of the sample increased to The melting point (Tm) reaches (550°C) .

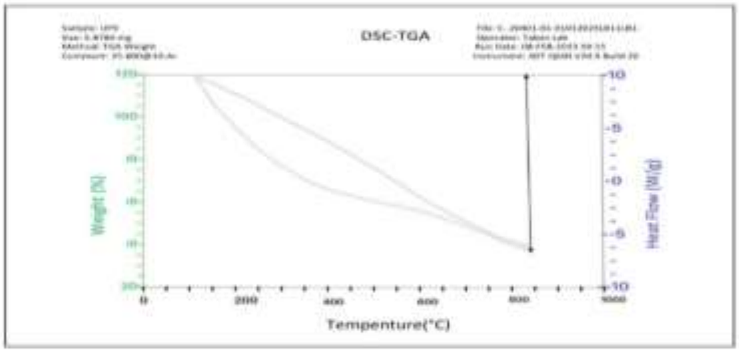
Table (13) shows the degree of glass transition, the melting point and the degree of crystallization in differential thermal analysis.

Samples	Tg (°C)	Tm (°C)
O + G	150	450
O + PE	170	550
O + PR	180	540

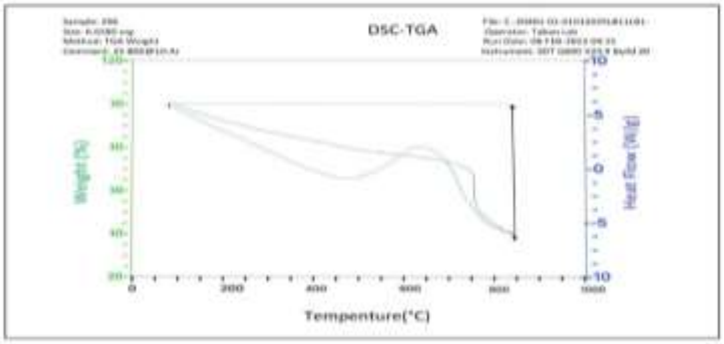
TG: Degree glass transition /Tm: Melting Point /Tc: Degree of crystallization



Figure(6) TGA and DSC curve of alkyd resin from olive oil with propylene glycol



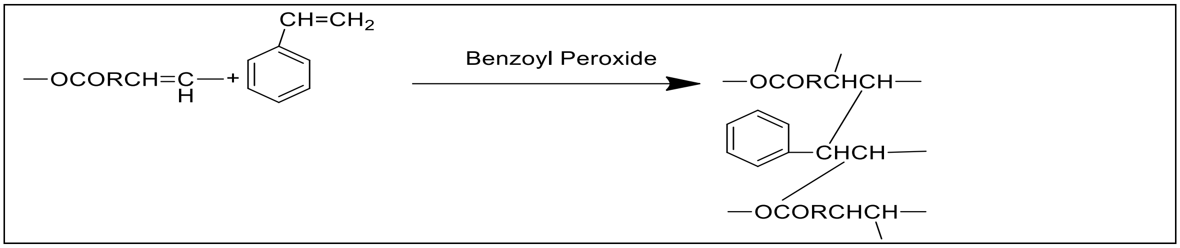
Figure(7) TGA and DSC curve of alkyd resin from olive oil with glycerol



Figure(8) TGA and DSC of alkyd resin from olive oil with Pentaerythritol

Synthesis and Characterization of styrenated alkyd resin

The styrenated alkyds were prepared by polymerization of the alkyd resin. The alkyds were withdraw into 100ml flask and heated in the presence of an initiator, benzoyl peroxide, under reflux at 120^0C for 3hrs in presence of N_2. According to the scheme (4):



Scheme (4) Synthesis of styrenated alkyd resin

FTIR spectrum of styrenated alkyd resin from Olive oil with glycerol

(O-G-S)

The FTIR spectrum of (O-G-S) which indicatesThe appearance of absorption band at (3300 cm^{-1}) for (OH) of Carboxylic acid. While the emergence of two distinct bands at the two frequencies (2854, 2923Cm^{-1}) is due to the vibration of the stretching of the aliphatic (C-H) bond, also the appearance of the peak at the frequency (1750Cm^{-1}) is due to the vibration of the stretching of the bond (C=O) in the ester group and peak at the frequency (1680Cm^{-1}) is due to the vibration of the stretching of the bond (C=O) in carboxylic group . Also, the appearance of the peak at frequency (1465 Cm^{-1}) is due to the vibration of the aromatic bond (C=C), and the appearance of the peak at frequency (1615 Cm^{-1}) is due to the vibration of the bond stretching (C=C) of the alkene, as well as the appearance of the peak at frequency (1110 cm^{-1}) to the (C-O) straining vibration. The band at 2135.62 cm^{-1} is due to carboxylic acid (RCOOH) group was indicated stretching at CO, also at peaks of 1321.513 cm^{-1} and1397.105 cm^{-1} methyl (CH_3) group [8-9-10].

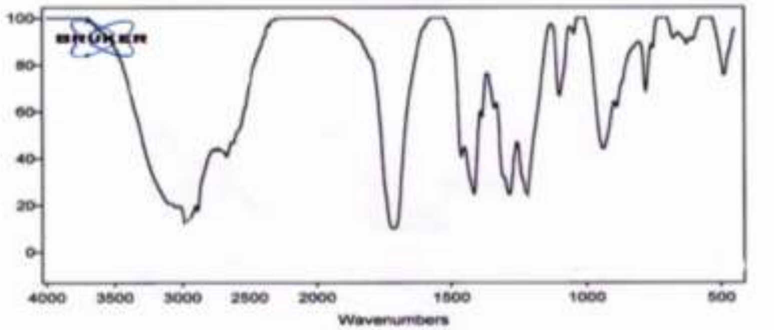


Figure (9) FTIR spectrum of styrenated alkyd resin from olive oil with glycerol

^{1}HNMR spectrum of styrenated alkyd resin from Olive oil with glycerol

(O-G-S)

^{1}HNMR) Spectrum of (O-G-S) assigns the following chemical shifts. Singles (δ= 0.5 ppm) for methyl group, singles (δ= 1.5ppm) for (CH_2), single (δ=2.5 ppm) for DMSO, singles (δ=7.7 ppm) for AR-H group, singles (δ= 3.4 ppm) for OCH_2, single (δ=11.5 ppm) for COOH. (δ= 5.3 ppm) indicates the presence of alcohol (RCHOH) group (OH) [8-9-10].

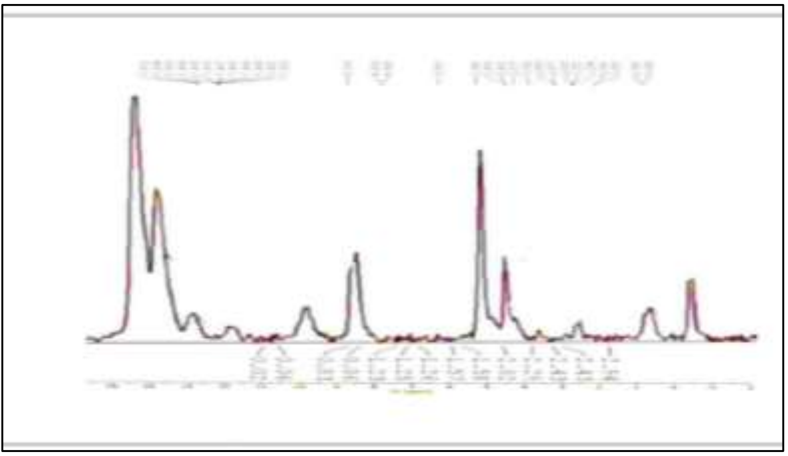


Figure (10) ^{1}HNMR spectrum of styrenated alkyd resin from olive oil with glycerol

FTIR spectrum of styrenated alkyd resin from Olive oil propylene glycol (O-PR-S)

The FTIR spectrum of (O-PR-S) which indicates the appearance of absorption band at (3300 cm^{-1} for (OH) of Carboxylic acid. While the emergence of two distinct bands at the two frequencies (2854, 2923Cm^{-1}) is due to the vibration of the stretching of the aliphatic (C-H) bond, also the appearance of the peak at the frequency (1750Cm^{-1}) is due to the vibration of the stretching of the bond (C=O) in the ester group and peak at the frequency (1680Cm^{-1}) is due to the vibration of the stretching of the bond (C=O) in carboxylic group . Also, the appearance of the peak at frequency (1465 Cm^{-1}) is due to the vibration of the aromatic bond (C=C), and the appearance of the peak at frequency (1615 Cm^{-1}) is due to the vibration of the bond stretching (C=C) of the alkene, as well as the appearance of the peak at frequency (1110 cm^{-1}) to the (C-O) straining vibration. The band at 2135.62 cm^{-1} is due to carboxylic acid (RCOOH) group was indicated stretching at CO, also at peaks of 1321.513 cm^{-1} and1397.105 cm^{-1} methyl (CH_3) group. This presence of unsaturated compounds is both resins and styrenated resins is an evidence that both alkyds and styrenated alkyds can dry at any a particular time [8-9-10].

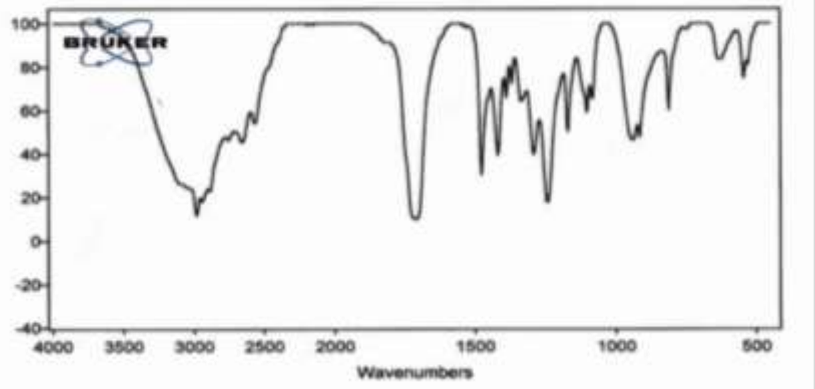


Figure (11) FTIR spectrum of styrenated alkyd resin olive oil with propylene glycol

^{1}HNMR spectrum of styrenated alkyd resin from Olive oil propylene glycol (O-PR-S)

^{1}HNMR) Spectrum of (O-PR-S) Singles (δ= 0.5-0.8 ppm) for methyl group, singles (δ= 1.2-1.6ppm) for (CH_2), single (δ=2.5 ppm) for DMSO, singles (δ=7.1 ppm) for AR-H group, singles (δ= 3.4 ppm) for OCH_2, single (δ=14 ppm) for COOH. (δ= 5.6 ppm) indicates the presence of alcohol (RCHOH) group (OH) [8-9-10].

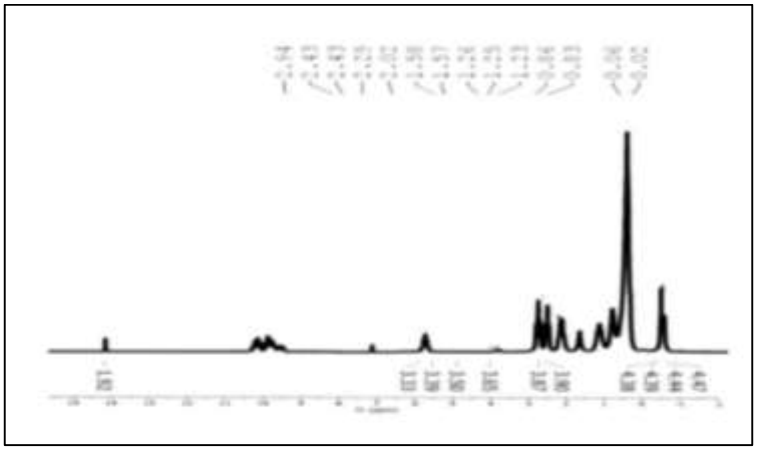


Figure (12) ^{1}HNMR spectrum of styrenated alkyd resin with olive oil with propylene glycol

FTIR spectrum of styrenated alkyd resin from Olive oil with Pentaerythritol (O-PE-S)

The FTIR spectrum of (O-PE-S) which indicatesThe appearance of absorption band at (3300 cm^{-1} for (OH) of Carboxylic acid. While the emergence of two distinct bands at the two frequencies (2854, 2923Cm^{-1}) is due to the vibration of the stretching of the aliphatic (C-H) bond, also the appearance of the peak at the frequency (1750Cm^{-1}) is due to the vibration of the stretching of the bond (C=O) in the ester group and peak at the frequency (1680Cm^{-1}) is due to the vibration of the stretching of the bond (C=O) in carboxylic group . Also, the appearance of the peak at frequency (1465 Cm^{-1}) is due to the vibration of the aromatic bond (C=C), and the appearance of the peak at frequency (1615 Cm^{-1}) is due to the vibration of the bond stretching (C=C) of the alkene, as well as the appearance of the peak at frequency (1110 cm^{-1}) to the (C-O) straining vibration. The band at 2135.62 cm^{-1} is due to carboxylic acid (RCOOH) group was indicated stretching at CO, also at peaks of 1321.513 cm^{-1} and1397.105 cm^{-1} methyl (CH_3) group [8-9-10].

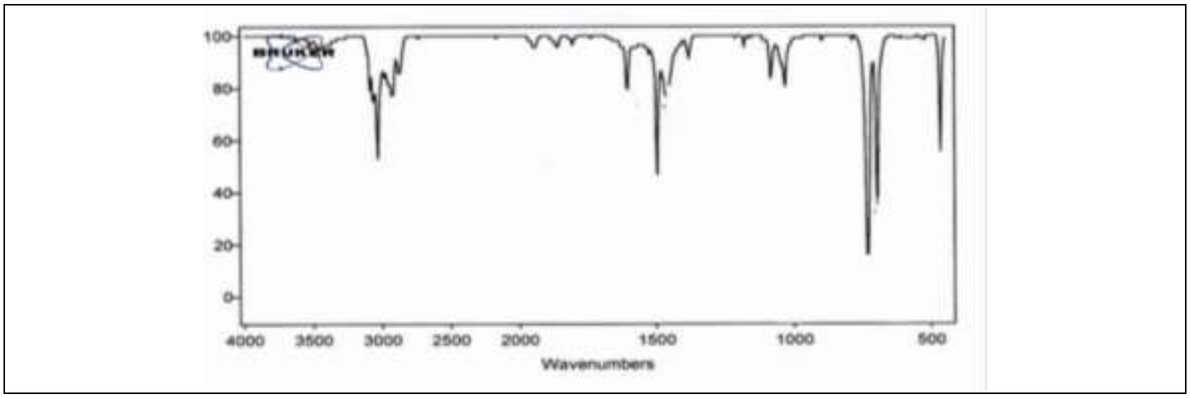


Figure (13) FTIR spectrum of styrenated alkyd resin olive oil with Pentaerythritol

^{1}HNMR spectrum of styrenated alkyd resin from Olive oil with Pentaerythritol (O-PE-S)

^{1}HNMR Spectrum of (O-PE-S) assigns the following chemical shifts. Singles (δ= 0.6 ppm) for methyl group, singles (δ= 1.2ppm) for (CH_2), singles (δ=7.1 ppm) for AR-H group, singles (δ= 3.4 ppm) for

OCH_2, singles (=13.4 ppm) for COOH. (= 5.6 ppm) indicates the presence of alcohol (RCHOH) group (OH) [8-9-10].

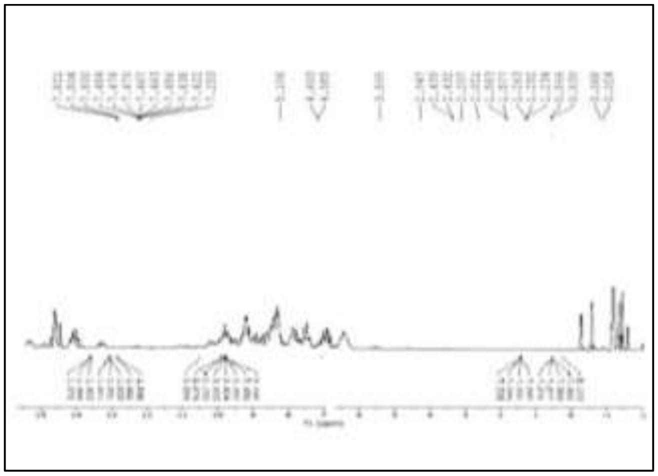


Figure (14) ^{1}HNMR spectrum of styrenated alkyd resin olive oil with pentayrethritol

Physical-chemical properties of styrenated alkyd resins

Copolymerization of styrene with olive oil-modified alkyd resin yields a transparent product with better impact strength, increased solvent resistance and higher softening point. In the study of polystyrenation process, the acid value does not change significantly as the reaction progresses. This shows that thermal polymerization did not occur under the reaction prevailing conditions. Only iodine and viscosity values change significantly as the reactions progress as shown in Table (14). There was an initial increase in the iodine values as the level of substitution increased instead of decreasing. This may be due to the double bonds in the styrene structure. But as the reaction proceeds after 1hr; it was observed that the iodine value decreased. This could be due to the consumption of the double bond as polymerization progressed. It is an expected result because double bonds are consumed during the reaction. The increase in viscosity throughout the reaction indicates the high level of cross linking. Their properties are quite comparable except their iodine values and viscosities. The decrease in the iodine values of styrenated alkyd resins was due to the consumption of the double bonds as polymerization progressed. The increase in the viscosity of styrenated resins could be as a result of high cross linking due to the presence of double bonds in the styrene structure.

Table (14) Show the physical-chemical properties of styrenated alkyd resins

Styrenated Alkyd resins	**Viscosity (CP)**	**Acid value (mg KOH g^{-1})**	**Iodine number (gI_2/100 g)**	**Density (gm/Cm^3)**
O-G-S	1886	10.3	97	0.97
O-PR-S	1624	10.2	100	0.96
O-PE-S	High V	10.5	101	0.98

Drying time

The steel panel used for evaluating the drying time of the styrenated alkyd resins was kept in vertical position after application of the resins. The results as presented in Table (15) reveal that drying time of the styrenated alkyd resin is higher than that of the un styrenated alkyds. Styrene monomers are known to increase the molecular weight [13], and with increase in molecular weight, fewer crosslinks are required to form coherent film [13], or to reach the drying stage [14]. The results further reveal that the drying time of the styrenated alkyds decreases with increase in styrene monomer content. The drying process occurs as a result of the occurrence of the oxidation and polymerization process of the alkyd resin, and the auto-oxidation mechanism is a complex process [15]. And there are more than one type of intermediates that can be formed, and the double bonds in fatty acids or vegetable oils may be conjugated or unconjugated, and the form of the double bonds has effects in drawing cross-linking [14,15], which is formed in the polymerization process. Alkyds based on unsaturated fatty acids and oils can be dried quickly because increased in the content of styrene which accelerates the oxidation of fatty acids. Moreover, in this case C-C bond type cross links are formed and the resulting films are more chemically resistant and durable than in case of air-drying systems where CO-O-C bond type cross links are formed.

Table (15) shows the drying time values for the prepared styrenated alkyd resins

Alkyd resins	Drying Time (min.)
S-G-S	10
O-G-S	35
O-PR-S	46
O-PE-S	25

Solubility: The styrenated alkyd resins based on olive show high solubility in different types of solvents as shown in Table (16). The solvents used in this test include benzene, toluene, xylene, acetone, DMSO, ethanol and methanol. Solvent molecules increase with the distance between the molecules chains of the resins and styrenated resins. The space between long chains with pendant side group of the resins and styrenated resins are invaded by solvent molecules as they fill the space made available by chain movements. When movements bring two chains close to proximity, short range attractive forces are therefore established resulting in restricted chain movement and thus the formation of a viscous system [16]. Solvents are added to deal with the problem of high viscous resins which is an obstacle in substrate's wet ability. One remarkable observation of the styrenated resins in these solvents is that the styrenated alkyd resins dissolve faster than. This could be due to the high viscous nature of styrenated resins. This high viscous nature of styrenated resins could be attributed to the high cross linkage in their structure.

Table (16) shows the solubility of styrenated alkyd resins Chemical resistance

nated Alkyd Resin	solvent							
	Xylene	DMF	Toluene	Acetone	DMSO	Benzene	Methanol	Ethanol
O + G + S	+	+	+	+	+	+	+	+
O + PR + S	+	+	+	+	+	+	+	+
O + PE +S	+	+	+	+	+	+	+	+

+ Soluble at room temperature

Chemical resistance

Their chemical resistance of alkyd resin showed that they are resistant brine, water and acids, but susceptible to alkali, as they were removed in alkali medium. Their drying schedule of the styrenated alkyd as revealed in Table (17) clearly shows an improvement from that of the pure alkyd, as they were set-to-touch in about 5 min, surface dry in one and a half hours. They were all completely dried in about two and half hours. This drying time was irrespective of the amount of styrene used in the co-polymerization. The chemical resistance of the styrenated alkyds is similar and also shows an improvement on the pure alkyd. Unlike the un styrenated alkyd which was only resistant to brine, water and acid, the styrenated alkyds also showed resistance to alkali. This therefore means that styrenation assisted in masking the ester linkages of the polyester from alkali hydrolysis.

Table (17) Show the chemical resistance of styrenated alkyd resins

Styrenated Alkyd Resin	Dist.H_2O	HCl	H_2SO_4	KOH	NaCl	THF
O + G + S	+	+	+	+	+	+
O + PR + S	+	+	+	+	+	+
O + PE +S	+	+	+	+	+	+

(+) denotes the insoluble resistant of styrenated alkyd resin

Thermogravimetric analysis (TGA) for styrenated alkyd resin

The thermal properties of the prepared styrenated alkyd resins were investigated by means of Thermogravimetric analysis (TGA) analysis in a Nitrogen atmosphere at a heating rate of 10°C/min and the results such as It, Ft., T50%, and char yields at 700°C are summarized in Table (18). The temperatures of 50% weight loss of polymers as a standard indication for thermal stability of styrenated alkyd resins were all above 560°C, which indicates excellent thermal stability of polymers. The stability of the polymer increased with the increase in content of aromatic rings. The char yields of styrenated alkyd resins at 700°C “between” 50% to 98% in nitrogen, which indicate they could meet high temperature resistant requirements as some special materials in fiber reinforcements, fire-retardants and curing agents.

Through TGA experiments, it was found that both rates of the first weight monomer. Then an endothermic behavior observed at high temperature region observed caused by crystallization. The study of styrenated and resins decomposition allows us to understand the thermal stability of the material, as well as direct us to the creation of new and better structures with greater thermal resistance.

The thermos grams of styrenated alkyd resins exhibits two distinct stages. One is in the range of 40-200˚C due to water loss and decomposition of styrenated alkyd resins low molecular weights, the other stage in the range of 250–550 ˚C. During industrial production of alkyds, there might be some oxygen present. In order to determine the oxidative thermal stability of the resin in these conditions. Because the thermal degradation was already pronounced at 250 °C. The extent of cross-linking between the polymer chains is expected to be reduced. These resins are mainly intended for applications in paint and ink formulation and therefore the lower thermal stability is not expected to be an issue because typical industrial processes proceed far below the degradation temperature. The styrenated alkyd resins exhibit three-stage thermal processes. But the values are different for each stage, the first group starts from (160,170 and 175) and the second group starts at (370,450 and 490) while the third group appears at (490,650 and700). With further increasing temperature to 250˚C, styrenated alkyd resins exhibits a second step decomposition implying the decomposition of carboxyl groups of polymer chains. The third decomposition step is suggested to be due to the thermal decomposition of the chain backbone [17].

Table (18): Thermal behavior data of styrenated alkyd resins

Samples	TGA (Ċ)					Residue % at 800 Ċ	Chart % at 600 Ċ
	T_i	T_{op1}	T_{op2}	T_f	$T_{50\%}$		
O + G + S	170	490	700	800	740	45	66
O + PR + S	175	450	650	800	720	45	96
O + PE +S	160	370	490	800	500	41	50

Differential Scanning Calorimeter Analysis (DSC) Study for the prepared styrenated alkyd resins:

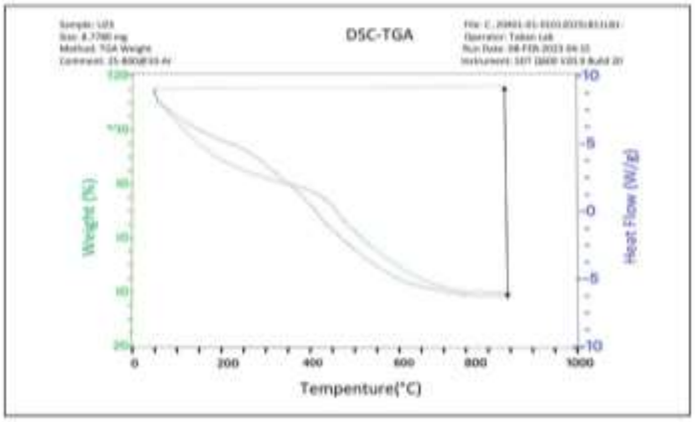
This type of analysis expresses the amount of energy absorbed from the sample during its heating and cooling or at a constant temperature. And the degree of crystallization (Tc) [18]. For a sample prepared from the interaction of styrenated of olive oil with glycerol shows, and the results showed the glass transition value (Tg) of the mixture (150°C), indicating an increase in the temperature flow, and then the sample absorption rate increased. For heat until it reaches the melting point (Tm) at (710°C).

For a sample prepared from the interaction of styrenated olive oil with propylene glycol shows, and the results showed the glass transition value (Tg) of the mixture (130°C), indicating an increase in the temperature flow, and then the rate of heat absorption of the sample increased to the melting point (Tm) reaches (550°C).

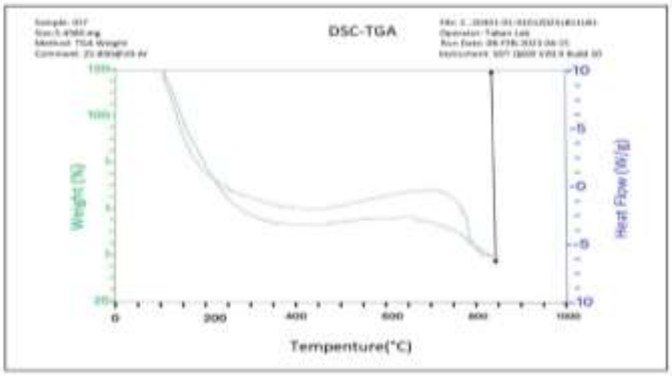
)for a sample prepared from the interaction of styrenated olive oil with Pentaerythritol shows, and the results showed the glass transition value (Tg) of the mixture (100°C), indicating an increase in the temperature flow, and then the rate of heat absorption of the sample increased to The melting point (Tm) reaches (410°C) .

Table (19) shows the degree of glass transition, the melting point and the degree of crystallization in differential thermal analysis of styrenated alkyd resin

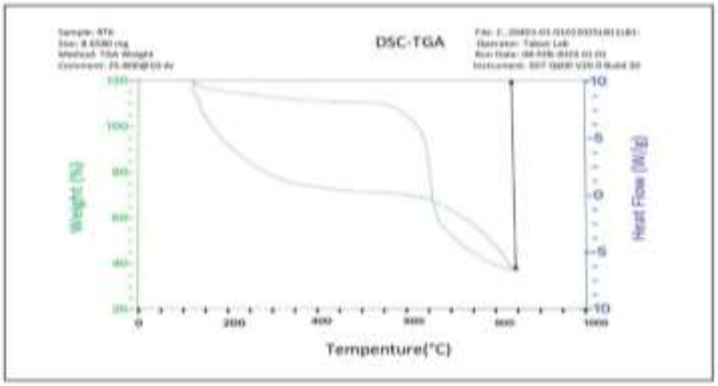
Samples	Tg (°C)	Tm (C°)
O + G + S	150	710
O + PR + S	130	550
O + PE +S	100	410



Figure(15) TGA and DSC curve of styrenated alkyd resin from olive oil with Pentaerythritol



Figure(16)TGA and DSC curve of styrenated alkyd resin from olive oil with glycerol



Figure(17) TGA and DSC curve of styrenated alkyd resin from olive oil with propylene glycol

CONCLUSION

Copolymerization of olive oil-modified alkyd resin with styrene by free radical polymerization has been established to have a major improvement on the coating properties of the resultant copolymer. Specifically, the resultant styrenated alkyd resins possessed better chemical resistance. This study also showed that longer reaction time gave a faster drying resin. The FTIR spectrum confirmed the chemical structures of the raw Olive oil, resins and styrenated resins with the functional ester groups present. Therefore, it can be concluded that styrenated alkyds offers an excellent potential applications in surface coating purposes

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