

SYNTHESIS AND CHARACTERIZATION OF NEW ALKYD RESINS (SHORT, MEDIUM AND LONG) BASED ON SUNFLOWER OIL AND LINOLEIC ACID AS BINDER FOR PAINTS

MOHAMMED AIL MUTAR¹ & NOOR MOHAMMED ABDUL HASSAN²

¹Professor, Department of Chemical Engineering, College of Engineering, University of AL-Qadisyia, Iraq ²Department of Chemistry, College of Education, University of Al-Qadissiya, Iraq

ABSTRACT

Alkyd resins include a very high proportion of common binders, which are used in the pants. New alkyd resins were synthesized by reacting (sunflower oil or linoleic acid with poly ethylene glycol or triethanol amine and phthalic anhydride) in the presence of lead oxide as a catalyst. The synthesis of alkyd resins included two stages. The first stage is to convert sunflower oil or linoleic acid to monoglycerides as a polyol by alcoholysis. Esterification process took place in the second stage through adding phthalic anhydride and xylene to the mixture. There were three different kinds of alkyd resins that have been synthesized (Short, medium and long) from sunflower oil or linoleic acid by using different ratios of phthalic anhydride. 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. Thermal analysis of alkyd resins is conducted by using thermo Gravimetric Analysis (TGA) and thermal differential calorimeter (DSC) techniques, which reveals that these Aromatic alkyd resins possess thermal stability. Alkyd resins were characterized by FT-IR and IHNMR spectroscopies.

KEYWORDS: Alkyd, Sunflower oil, Linolinic acid, Paint & Binder

Received: Dec 23, 2016; Accepted: Jan 06, 2017; Published: Jan 21, 2017; Paper Id.: IJCPTFEB20171

INTRODUCTION

Paints may possibly be described as a colloidal combination of chemical ingredients, when diffused on a surface in a thin layer they form a dense, consistent and adherent layer. They are used regularly in our life for ornamental purposes, and for preventing surfaces of being affected by different environmental influence as UV-radiation, chemical invasion and mechanical stresses. A binder, pigment, solvent, and additives are common ingredients of paint. The polymer-binding material (alkyd resin) is responsible in addition to wide range of variations for finding a continuous layer that adheres to the lower layers and binds other ingredients together ^{(1).} Coating material through using Polyester or alkyd is commonly employed for surface covering as binders, adhesives and plasticizers. What is interesting about Alkyd is that it is the lowest materials in cost if compared with other coating materials and it is subject to give a covering that shows less layer faults during applications. Also, stability of alkyd layers, particularly for outdoors use, tends to be poorer than films, i.e., acrylics and polyurethanes ^(2, 3). However, one of the factors affecting coating flim properties is the type of fatty acid or oil used in the alkyd production ^(4, 5). Various types of oil can result in differences in film properties. The preparation of

alkyd resins can be achieved by condensation polymerization of a polyhydric alcohol (e.g. glycerol) and polyfunctional acid or polybasic acids (e.g. phthalic anhydride and isophthalic acid) changed by oily acid or their triglyceride. The alkyd resins manufactured this way are known as oil-modified alkyd resins and form 70% of the common binders used in external coating ⁽⁶⁾. They define the performance quality of surface coatings such as the degree of drying, gloss, stability of the dry layer and resistance of the dry layer to scratch and chemicals. However, categorizing of alkyd resins is centered on the oil length and oil type ⁽⁷⁾ The vegetable oils, which used in oil-modified alkyd resins are typically extracted either by a mechanical press or solvent extraction⁽⁸⁾. The natural oil in the oil-modified alkyds reacts with atmospheric oxygen, which leads to the formation of a network of polymers cross-linked through the (C=C) bond. The oil oxidative drying brings about the formation of a layer that displays enhanced characteristics with drying time, hardness or water resistance ⁽⁹⁾. Alkyd resins have gained high significance due to their economy, availability of raw materials, biodegradability, durability, flexibility, good adhesion and ease of application. In this work, two alkyd resin (AR₁-AR₂) have been synthesized in high yield by polycondensation between dicarboxlic acid and polyols with oils using lead oxide as catalyst. Qualitative structure analysis of the polymers have been carried out by the using of FT-IR, and ¹HNMR spectroscopy, thermal stability were systematically investigated.

EXPERIMENTAL

Materials

Sunflower oil, linoleic oil, phthalican hydride, lead oxide, xylene, all from (MERCK); Poly ethylene glycol, Tir ethanol amine, Ethanol, (Scharlab S.L) ; Tetrahydrofurane (THF), Dimethyl sulphoxide (DMSO), all from (MERCK) ; Methanol, Acetone, Toluene, Carbon tetrachloride, all form (BDH-chemicals) ; Sulfuric acid form (Sd fine-CHEM) ; Hydrochlo-ric acid, Sodium chloride, all form (Hi-media) ; potassium hydroxide, potassium Iodide, Sodium thiosulfate all from (HIMEDIA).

Instruments

FTIR 8400S, Fourier Transform infrared spectrophotometer, SHIMADZU, Japan), (Oven, Trivp International Crop. Italy),(Hot plate stir, BibbyStrlintd.UK) (Measurement of 1 HNMR Spectra : recorded NMR spectra using a type of Bruker, Ultra shield 300 Mhz, Switzerl and using (DMSO-d6) as a solvent at the university's Educational teacher-Tehran Iran),(Thermogravimetry analysis (TGA) were performed on a polymer laboratories co England, Model pL-TG at Iran polymer & petrochemical institute, using a heating rate of 10°C/min in Argon atmosphere within the temperature range of 25-800°C)(differential thermal analysis (DSC) measurement using apparatus (DSC) type (DSC 131 Evo, SETARAM) is the origin (France) in the Department of Chemistry / Faculty of Education / University of Qadisiya), (viscosity device The use of viscosity measurement device for measuring the viscosity of the alkyd resin models record in the Department of Chemistry / Faculty of Education / University of Qadisiya), type (RVDV- II + P 8500), (230 V~) and frequency (50/60 Hz) and strongly (30 VA). The machine is manufactured in (U.S.A).

Synthesis of Alkyd Resin

Oil modified alkyd resin was prepared from Sunflower oil with Poly ethylene glycol or linoleic acid with triethanol amine and phthalic anhydride using PbO as catalyst. The preparation was done in a 4-neck round bottom flask fitted with a motorized stirrer, a nitrogen inlet, a thermometer pocked and a hold for sampling. In the preparation of alkyd

resin, two stages were involved. The first stage was alcoholysis stage and the second stage was esterification stage.

Raw Material	Short	Medium	Long
Sunflower oil Or linoleic acid	25-40 %	45-60 %	60-70 %
Phthalic anhydride (PA)	35>gm	30-35 gm	20-30 gm
Glycerol (G)	14.6 gm	14.6 gm	14.6 gm
Lead oixd	0.4 gm	0.4 gm	0.4 gm
Xylene	60 ml	60 ml	60 ml

Table 1: Shows the Proportions of the Chemicals used in the Reaction

Stage 1 (alcoholysis): In this stage, monoglyceride was first prepared by reacting (the sunflower oil with poly ethylene glycol or linoleic acid with triethanol amine), then added PbO as a catalyst. In alcoholysis reaction, the oil was heated with an agitation speed of (700 rpm) and N2 sparging rate of about (0.06ft3/sec) to 230-240°C. Alcohol and selected catalyst were added and alcoholysis reaction was carried out at 230-240°C. The reaction of the mixture continued tillthe sample of the reaction mix became solvable in two to four volumes of anhydrous methanol. After completing alcoholysis reaction, the reaction mixture was cooled to 140°C.

Stage2 (esterification): In this stage, phthalic anhydride was added to the monoglyceride mixture. The temperature was maintained at the range of 230-240°C and maintained at this temperature. The leakage amount of N2 was increased to (0.1ft3/sec). The reaction was observed by intermittent determination of the acid value of the mixture till acid value fell to nearly (9).

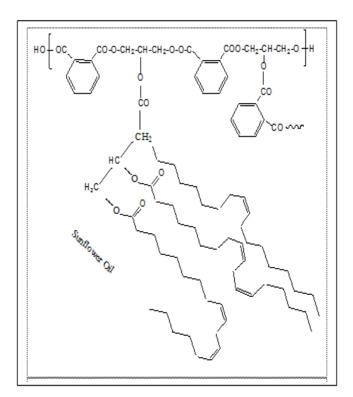


Figure 1: Structure of Polymer (AR1)

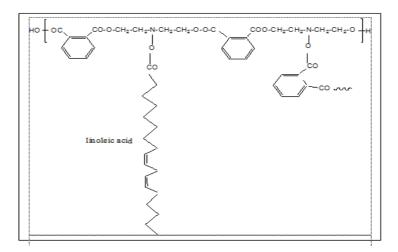


Figure 2: Structure of Polymer (AR2)

Physico – Chemical Tests

Acid Value Test

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

Drying Test

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

Saponification Number Test

Weight (1 gm) of sample into an Erlenmyer 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 erlenmyer flask, 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) HCl (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.

Iodin Number Test

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 Hanus solution, and seal. Shake for one minute, then keep it sealed and leave in a drak 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)mol / L sodium thiosulfate to obtain iodine value then also perform blank test to obtain blank level.

Density Test

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

Synthesis and Characterization of New Alkyd Resins (Short, Medium and Long) Based on Sunflower Oil and Linoleic Acid as Binder for Paints

Viscosity Test

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

Volatile Matter Test

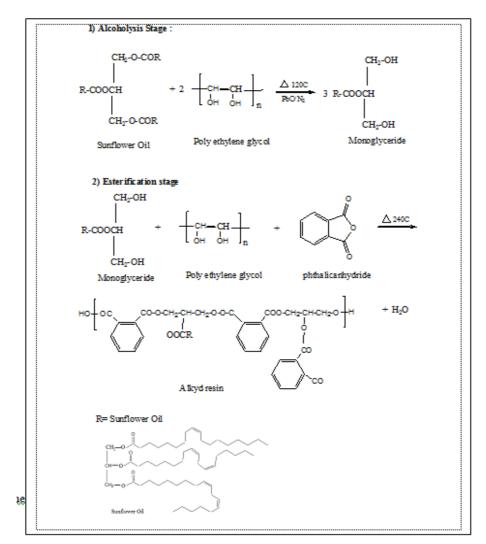
Three specimens were placed in the oven within (30) min after preparation of alkyd resin in previously weighed watch glass and heated for (2 h) at (135-140) °C. The Nonvolatile matter was calculated from the difference in initial and final weights of the watch glass. The mean value of the three results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

RESULTS AND DISCUSSIONS

Synthesis and Characterization of Polymers Prepared

Synthesis and Characterization of (AR1)

This polymer was synthesized by the condensation of sunflower oil with Polyethylene glycol and phthalic anhydride in the presence of lead oxide as catalyst and temperature is $(120-240 \text{ c}^{\circ})$ for (6 hours) according to the equation in the reaction scheme (1).





Characterization of (AR1)

FT-IR Spectrum

The FTIR spectra of (AR1) as show in (Figure 3) which indicates absorption band of (OH) Carboxylic at (3018 cm-1), (C-H) aromatic at (3008 cm-1), (C-H) aliphatic at (2854, 2923 cm-1), (C=O) in the ester group at (1743 cm-1), (C=C) aromatic at (1465 cm-1), and (C-O) at (1110 cm-1).

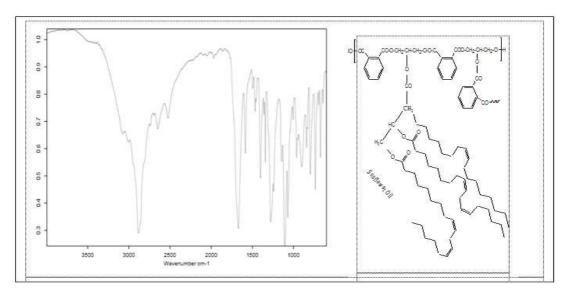


Figure 3: FTIR Spectra of (AR1)

(1H-NMR) Spectrum of (AR1), is shown in Figure (4) assigns the following chemical shifts ; (\Box = 1.15-1.22 ppm) for methyl group, (\Box = 2.20-2.25 ppm) for (CH2), (\Box = 2.49-2.60 ppm) for (OCH2), (\Box = 2.5 ppm) for (DMSO), (\Box = 3.34 ppm) for (H2O), (\Box = 7.04-7.12 ppm) for Ar-H group

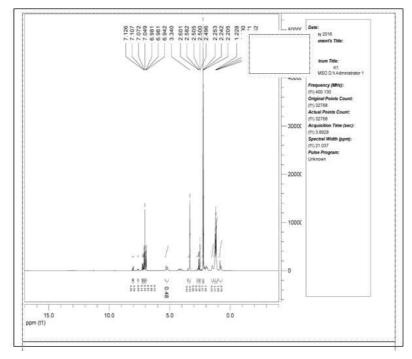
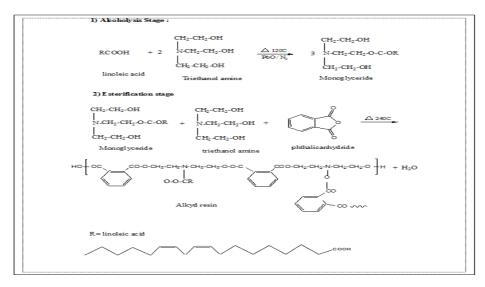


Figure 4: 1HNMR Spectra of (AR1)

Synthesis and Characterization of New Alkyd Resins (Short, Medium and Long) Based on Sunflower Oil and Linoleic Acid as Binder for Paints

Synthesis and Characterization of (AR2)

This polymer was synthesized by Condensation of linoleic acid with tri-ethanol amine and phthalic anhydride in the presence of lead oxide as catalyst and temperature is $(120-240 \text{ c}^{\circ})$ for (6 hours) according to the equation in the reaction scheme (2).



Scheme 2: Synthesis of (AR₂)

Characterization of (AR₂)

FT-IR spectrum : The FTIR spectra of (AR₂) as show in (Figure 5) which indicates absorption band of (OH) carboxylic at (3020 cm-1), (C-H) aromatic at (3001 cm-1), (C-H) aliphatic at (2854, 2923 cm-1), (C-N) at (1257 cm-1), (C=O) in the ester group at (1735 cm-1), (C=C) aromatic at (1458 cm-1), and (C-O) at (1257 cm-1).

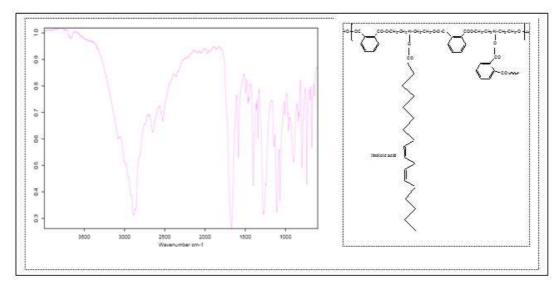
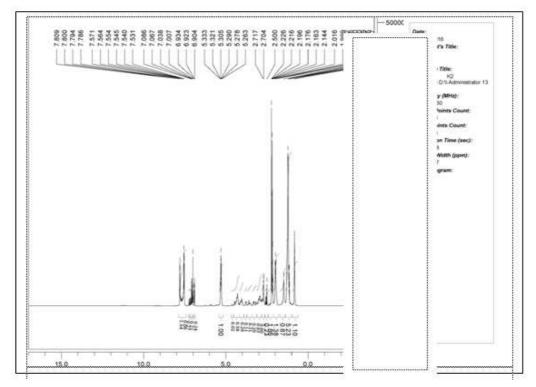


Figure 5: FTIR Spectra (AR₂)

(¹H-NMR) Spectrum of (AR₂), is shown in Figure (4) assigns the following chemical shifts ; (δ = 0.81-1.23 ppm) for methyl group, (δ = 1.96-2.22 ppm) for (CH₂), (δ = 2.270-22.271 ppm) for (OCH₂), (δ = 2.5 ppm) for (DMSO),



(δ = 5.26-5.33 ppm) for (OH), (δ = 6.90-7.08 ppm) for Ar-H group, (δ = 7.53-7.80 ppm) for NH₂ group.

Figure 6: ¹HNMR of (AR₂)

Physico – Chemical Tests

Acid Value Test

The acid value (AV)is the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize one gram of chemical substance. The acid number is a measure of the amount of carboxylic acid groups in a chemical compound, such as a fatty acid. It has been observed from the results shown in the (table 2), (AR₁) prepared from sunflower oil showed an acid value higher than the (AR₂) prepared from linoleic acid due to the length of the fatty acid chain component there of resin sunflower oil, containing (C_{57}) carbon atom and linoleic acid containing (C_{18}).

Table 2: Shows the Acidic Alkyd Resins Prepared Values

Alkyd Resin	Short	Meduim	Long
AR_1	9.25	9.53	9.81
AR_2	7.85	8.13	8.72

IODIN Number Test

The value of Iodine in chemistry is calculated through the mass of Iodine in grams, which is used by 100 grams of a chemical substance. The numbers of Iodine are regularly employed to define the extent of unsaturation in oily acids. This unsaturation takes the form of double bonds that reacted with Iodine compounds. The higher the Iodine number, the more C=C bonds are present in the fat (note that the number of iodine saturated fatty acids equals zero). As well as the number of Iodine used in the to detect adulterated vegetable oils with oils constants. Whenever a high Iodine number, i.e. it contains high proportion of unsaturated fatty acid and iodine number and if Iodin number islow, i.e. fatty acids is saturated. The results of the prepared resins observed through the (table 3), The Iodine value is higher in (AR₁) than (AR₂)

Synthesis and Characterization of New Alkyd Resins (Short, Medium and Long) Based on Sunflower Oil and Linoleic Acid as Binder for Paints

because of chain unsaturated oil fatty length of sunflower (C_{57}) in (AR₁) while linoleic acid (C_{18}) short chain fatty acid in (AR₂).

Alkyd Resin	Short	Medium	Long
AR ₁	171	164	156
AR ₂	150	144	136

Table 3: Shows the Values of Iodine Number Alkyd Resins Prepared

Saponification Value Test

Saponification value represents the number of milligrams of potassium hydroxide required to saponify (1g) of fat under the conditions specified. This is to measure the average molecular weight (or chain length) of all the fatty acids presented in this process. Most of a fat mass of /tri-ester are in the 3 fatty acids, it permits for comparison of the average fatty acid chain length. The long chain of fatty acids, which are found in fats have low saponification value due to their relative fewer number of carboxylic functional groups for each mass unit of the fat when compared to short chain fatty acids. The results were observed from the (table 4) showed (AR₁) prepared from sunflower oil(C₅₇) less saponification value than (AR₂) prepared from vegetable oil short-chain linoleic acid (C₁₈) because of the saponification number proportional inversely to the length of chain fatty acid.

Table 4: Shows the Value Saponification Alkyd Resins Prepared

Alkyd Resin	Short	Medium	Long	
AR_1	193	190	187	
AR_2	196	191	188	

Density Test

A substance density and the volumetric mass density is its mass per unit volume. Mostly used symbol for density is ρ . and depends on temperature and pressure. The results were observed for the resins prepared in the(table 5), The density is less of alkyd resin increasing fatty acid chain length and vice versa, also due to the presence of a relatively less number of active carboxyl groups. Is observed (AR₁) prepared from sunflower oil (C₅₇) showed the density is less than (AR₂) prepared from linoleic acid (C₁₈).

Table 5: Shows the Intensity Values Alkyd Resins Prepared

Alkyd Resin	Short	Medium	Long
AR_1	0.796	0.791	0.786
AR_2	0.858	0.853	0.848

Drying Test

Drying rate of alkyd resin based on sunflower oil or linoleic acid of diverse applied thickness and employed certain amount of cobalt. These oils categorized as non-drying oil that contain fatty acid higher proportion in saturated chains than other types of oil. Non-drying oil alkyds do not produce layer without alteration ^{(10).} However, alteration and addition of driers provide resins the form of film at regular atmospheric circumstance. Denser layers (120 μ m) are in need for much more time to dry in comparison with thinner layers (30 μ m). The thicker films drying mechanism necessitate a great deal of cobalt to cross-link between chains. When the catalyst concentration decreased, a less dense cross-linked network was formed. The thicker films alkyd drying time can radically increase the oxygen uptake either at the double bond or methylene group as the increasing presence of driers⁽¹¹⁾. It was noted that the resin ability to air dry is because

phthalic anhydride modification in specific amount and drier that leads to resin to cross link. The higher the presence of phthalic anhydride and the driers, the longer chain length and a higher cross linked dense resin through condensation polymerization. The resin turns to be denser, viscous and more compact conferring self curing feature. The results were observed from the (table 6) showed Higher oil content in long oil and medium oil alkyds gave slower initial drying, due to more thermosetting of long oil alkyd as compared to short oil alkyd. Subsequently, better thorough drying can be assigned to same thermosetting nature of oil present in long oil alkyd. Short oil alkyd thus has slower thorough drying due to less oil present.

Alkyd Resin	Short	Medium	Long
AR_1	30min	45min	56min
AR_2	17min	23min	35min

Table 6: Shows the Values of the Drought Resins Prepared Time

Viscosity Test

The viscosity of a fluid is a measure of its resistance to gradual deformation by shear stress or tensile stress. For liquids, it corresponds to the informal concept of "thickness". The viscosity of the solution is an important tool for characterization polymers are a measure of molecular weight of polymer as the viscosity of the solution is a measure of the size. The factors affecting viscosity:

- Pressure: Pressure viscosity little importance but viscosity effect appears when the pressure increases (68 bar).
- **Temperature:** When temperatures decrease viscosity because at high temperature of liquid increase distances between molecules less friction and therefore less viscous. It is noted that the viscosity resins alkyd increases during reaction for all types of oils used in manufacturing, and also notes that the viscosity increase slowly during the hours (2-3) interaction. Then, it increases viscosity significantly in esterification reaction between mono glyceride and phthalic anhydride however after 5 or 6 hours ends interact very viscous alkyd resin consists of any strings are A gelatinous substance polymer (gelatin).
- The viscosity is highly dependent on amount of cross-linking in polymer. It was noted by the results shown in (table7), showed (AR₁) prepared from sunflower oil (C₅₇) less viscosity than (AR₂) prepared from vegetable oil short-chain linoleic acid (C₁₈) because of the viscosity proportional inversely to the length of chain fatty acid.

Alkyd Resin	Short	Medium	Long	Speed	No. Spendle	Temper.
AR ₁	110	100	90	100	6	25
AR ₂	180	160	140	50	0	25

Table 7: Shows the Viscosity Resins Prepared Values

Volatility Matter Test

It was noted by the results shown in (table 8), where the difference in the value of the volatility between each resin prepared (AR_2) showed less value volatility due to the short chain fatty acid (linoleic acid) while (AR_1) showed a high value volatility due to length chain fatty acid sunflower oil container in structure on the double bonds of the ability to interact with oxygen therefore volatility quickly.

Alkyd Resin	volatile
AR ₁	% 98
AR_2	%65

Table 8: Shows the Values of the Volatility of the Resins Prepared

Chemical Resistance Test

The resistance of the alkyd was determined in two media, distilled water and NaOH solution (Table 9), described that there was no effect on alkyd film after immersion in distilled water for 18 hours, was sufficient time to examine the water resistance. When the alkyd film was immersed in strong alkali solution, 3N NaOH, the film got whitening after immersion time for 8 hours, blistering after immersion for 16 hours and removal after immersion time of 24 hours. So the result shows that sunflower oil and linoleic acid modified alkyd resin have high chemical resistance.

Table 9: Shows the Chemical Resistance of the Resin Prepared Values

Alkyd Resin	NaOH	Distilled Water
AR_1	-	_
AR ₂	+	_

(-)Refers to Alkyd resins insoluble resistance

(+) Refers to Alkyd resins insoluble resistance

Solubility Test

Alkyd resins showed high solubility in different type of solvents.(table 10) described solubility of samples, was measured by taking the solubility (0.01 g) of the sample prepared resin and melted in (2 ml) of the solvent, The solvents used include (DMF, Acetone, Toluene, Xylene,) (Polar aprotic) non-polar solvents such as (Benzene, CHCl₃) and other solvents such as methanol, ethanol. The solvent molecules increase with the distance between the molecular chains of the resin. The spaces between long chains with pendant side group of resin 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 ^(12, 13). Solvent are added to deal with the problem of high viscous resin which is an obstacle in substrates wet ability.

Table 10: Shows the Solubility of Alkyd Resins

Alkyd		Solvent								
Resin	Xylene	DMF	Toluene	Acetone	DMSO	Benzene	Methanol	Ethanol		
AR_1	+	+	+	+	+	+	+-	+-		
AR ₂	+	+	+	+	+	+	+	+		

(+) soluble at room temperature

(+ -) partially soluble

Thermo Gravimetric Analysis (TGA) Study

Thermo gravimetric Anaylysis (TGA) involves determining changes in mass as a function of temperature. It is commonly used to search degradation temperatures, absorbed content of materials, levels of inorganic and organic parts contained in a material and anaylsis solvent residues. It employs a sensitive electronic balance from which the sample is suspended in a furnace controlled by a temperature programmer. The thermal properties of two samples of these alkyd resins were investigated by means of thermo gravimetric analysis (TGA) in Argon atmosphere at heating rate of 10 °C/

min. The results such as T_{i} , T_{op} , T_{f} , $T_{50\%}$, % Residue at 300 °C, and char yields at 200 °C are summarized in (Table 11). The temperatures of 50% weight loss of (AR₁, AR₂) as a standard indication for thermal stability of polymers were all from 300 °C, The char yields of (AR₁) are 74% and (AR₂) are 81% at 200 °C in Argon atmosphere, which indicate they could meet temperature resistant requirements, which can be used in surface coating application. Weight residue of (AR₁) are 51% and (AR₂) are 52% at 300 °C.

		DI	Г/• <i>С</i>			Residue	Char %
Alkyd Resin	\mathbf{T}_i	T _{op1}	T _{op2}	\mathbf{T}_{f}	T _{50%}	at °C300	at 200•C
AR_1	201	150	252	>300	>300	51%	74%
AR_2	190	150	250	>300	>300	52%	81%

 Table 11: Some Thermal Stability Characteristics Curves

 Thermal Gravimetric Analysis (TGA) of Alkyd Resins

DT: Decomposition temperature.

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 200 ° C: Residual weight percentage at 200 ° C in Argon by TGA

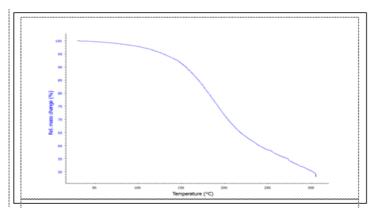


Figure 7: TGA Cure of AR₁

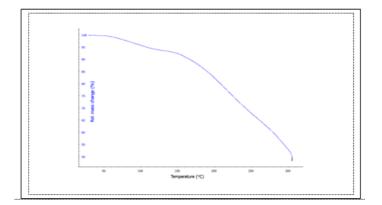


Figure 8: TGA Cure of AR₂

Differential Scanning Calorimeter Analysis (DSC) Study

Differential Scanning Calorimetry, is a technique of thermal analysis that investigates how material's heat capacity (Cp) is transformed by temperature. A known mass sample is heated or cooled and the variations in its heat capacity are observed as alterations in the heat flow. This allows to reveal transitions such as melts glass transitions (Tg), and the melting point (Tm) the degree of crystallization (Tc) ⁽¹⁴⁾. this test was applied to the prepared samples, Shows the (curve 9) for the sample came from reaction sunflower oil with Polyethylene glycol The results showed the value of the glass transition (Tg) of the mixture (36.41c °), referring to obtain the flow temperature and then increases endothermic the sample to reach the melting point (Tm) at (300 c °) completely dissolve and then less the sample heat absorption rate and by a curved appointed degree of crystallization (Tc) of the mixture was (167.4 c °) It also shows a (curve 10) for the sample came from reaction linoleic acid with triethanolamine and the results showed the value of the glass transition (36.3c°) referring to an increase in the flow temperature and then increase endothermic the sample to reach the melting point (Tm) at (295 c °) completely dissolve and then less the sample heat absorption rate and by a curved appointed degree of crystallization (Tc).

Table 12: Show	vs the Degree	of Glass T	'ransition, l	Melting Poir	it and the
Degree of	Crystallizatio	on in the Di	ifferential '	Thermal Ana	alysis

Samples	$Tg(c^{o})$	Tm (c°)	Tc (c ^o)
AR_1	36.41	300	167.4
AR_2	36.3	295	77.1

Tg: Degree glass transition

Tm: Melting Ponit

Tc: Degree of crystallization

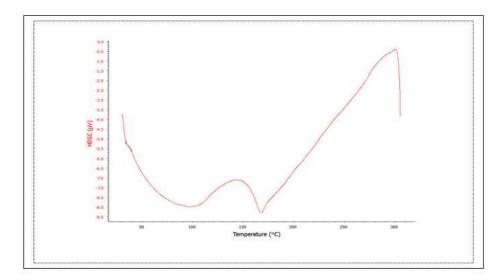


Figure 9: DSC Cure of AR₁

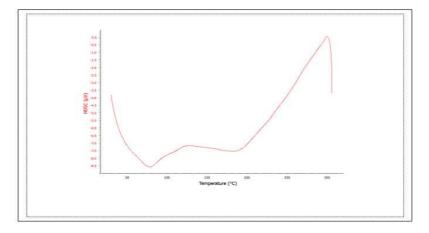


Figure 10: DSC Cure of AR₂

CONCLUSIONS

In this work, new alkyd resin used in many industries like paints and surface coatings because of their properties such as friction resistance, humidity, scalability high adhesion, high dry without addition a drying agent, and high flexibility. And It shows that through the study of their properties such as drying times, the volatility, saponification number, iodine number, acid value, and density of these resins all of the tests depends on the fatty acid chain length or type of vegetable oil used in the manufacture of these resins. Alkyd resins show high solubility in various solvents because their structures contain chemical groups such as (hydroxide, and links ethers) alkyd resins showed curves thermal gravimetric analysis (TGA) high increase in thermal stability because of the different types of vegetable oils used in alkyd resins industry and structural diversity of the structures of the new alkyd resins.

REFERENCES

- 1. Wicks, Z. W., Jones, F.N., &paappas, S.P. (1994). Organic coatings : science and technologe Vol. 1., John Wiley & Sons.
- 2. Zeno, W.W., Frank, N.J. and peter, S.p., Organic Coatings Science & Technology, 2nd Ed., Wiley Interscience, pp.135 and pp.142(1996).
- 3. Kim, D. and Kim, S.W.,; Barrier property and morphology of polypropylene / pol-yamide blend film^{*} Korean J. Chem. Eng., 20,776 (2003).
- 4. Kabasakal, O.S., Guner, F.S., Erciyes, A.T. and Yagci, Y.,, Styrenation of oils based on secondary esters of caster oil," J. Coating Technol., 67,47 (1995).
- 5. Kabasakal, O.S., Guner, F.S., Arslan, A., Ergan, A., Erciyes, A.T. and Yagci, Y.,, 'Use of caster oil in the preparation of various oil-based binders' J. Coating Technol., 68,57 (1996).
- 6. Bajpai, M., & Seth, S. (2000). Use of unconventional oils in surface coating blends of alkyd resins with epoxy esters. Pigment Resins Technol., 29,82-87. http://dx.doi.org/10.1108/03699420010317825.
- Micciche, F. (2005). The combination of ascorbic acid derivative/iron salts as catalyst for the oxidative drying of alkyd-paints
 : A Biomimetic approach. TechnischeUniversiteit Eindhoven. http://Alexandria.tue.nl/extra2/200512801.pdf
- Abulude, F.O., Ogunkoya, M.O., & Ogunleye, R.F. (2007). Storage properties of oils of two Nigeria oil seeds Jatrophacurcas (physic nut) and Helianthus annuus (sunflower). Amer. J. Food Tech., 2, 207-211. http://dx.doi.org/10.3923/ajft.2007.207. 211.

- 9. Akintayo, C.O. (2004). Synthesis and Characterization of Albiziabenth medium oil modification of alkyd resin and its chemically modified derivatives. phD thesis. University of Ibadan, Nigeria.
- 10. Issam A.M., Cheun C.Y., 2009. A study of the effect of oils on the properties of a new alkyd resin. Malaysian polymer Journal, 4(1), 42-49.
- 11. Akintayo, C.O., and Adebowale, K.O., 2004, Syntheses Characterization and Evaluation of Chlorinated Albiziabenth medium oil Alkyds, progress in Organic Coatings. 2 pp 138-143.
- 12. Boxall, J. and Von Fraunhofer, J.A., 1977. Concise paint Technology, Elek Science London.
- 13. Boxall, J. and Von Fraunhofer, J.A., 1980. Concise paint Formulation, principleand practice, George Godwin Limited London.
- 14. Bernhard wunderlich. Thermal Analysis, text for an audio course. ATHAS, Advanced Thermal Analysis, A laboratory for Research and Instruction (1981).