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Research Article

Synthesis and characterization of alkyd resin based on soybean oil and glycerin using zirconium octoate as catalyst

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ABSTRACT

A one pot synthesis of alkyd resins based on the soybean oil and glycerin with the zirconium octoate (zirconium 2-ethyl hexanoate) as a new renewable raw material was performed. The alcoholysis reaction of soybean oil and glycerin carried out in absence of nitrogen gas inlet in the presence of zirconium octoate. The alkyd resin was obtained from polycondensation of the alcoholysis products with phthalic anhydrid at 250 °C. The structure confirmed by FT-IR and H^1-NMR spectroscopy. Flexibility, drying time, hardness, adhesion test, impact resistance, gloss test and chemical resistance of synthesized alkyd resins was invesitigated. The prepared resin was formulated in white lacqure and yellowing resistance tested with commercial resins.

Keywords: Phthalic anhydride, soybean oil, zirconium octoate, alkyd resin.

Kataliz olarak zirkonyum oktoat kullanarak soya fasülyesi ve gliserin esaslı alkid reçinenin sentezi ve karakterizasyonu

ÖZ

Yeni bir yenilenebilir hammadde olarak soya fasulyesi yağı ve gliserin ile zirkonyum oktoat (zirkonyum 2-etil heksanoat) içeren alkid reçinelerinin tek bir saksı sentezi gerçekleştirilmiştir. Soya fasulyesi yağı ve gliserinin alkoliz reaksiyonu azot gazı olmaksızın zirkonyum oktoat varlığında yapıldı. Alkid reçinesi 250 °C' de alkoliz ürünlerinin ftalik anhidrit ile polikondenzasyonundan elde edildi. Yapı FT-IR ve H^1-NMR spektroskopi ile teyit edildi. Sentezlenen alkid reçinelerinin esneklik, kuruma süresi, sertlik, yapışma testi, darbe direnci, parlaklık testi ve kimyasal mukavemet özellikleri araştırıldı. Hazırlanan reçine beyaz lakürde formüle edildi ve sararma direnci ticari reçineler ile test edildi.

Anahtar Kelimeler: Ftalik anhidrit, soya fasülyesi yağı, zirkonyum oktoat, alkid reçinesi.

1. INTRODUCTION

Alkyd resins make an important group of commercial synthetic polymers and are used widely in coating and paint industry. They have become essential raw material in the production of metals, wood and wood-based materials like furniture and floors, cement, cement-lime and gypsum plasters. The commonly used raw materials for the production of alkyd resins, besides plant oils like soybean oil and linseed oil, are synthetic pentaerythritol, glycerin and phthalic anhydride which are toxic.[1] Alkyd resins can be defined in brief as polyesters modified with fatty acids, fatty oils or higher synthetic carboxylic acids. The molecules consist of a polyester backbone, which may be scarcely moderately branched depending on the raw material selected, and fatty acid groups as side chains excess (free) hydroxyl and residual carboxyl groups are also present. An alkyd resin consisting of oil solely, additional glycerol and ortho – phthalic acid represented in simplified form have produced industrially in 1930. Alkyd resins rapidly developed into the most important type of synthetic resin for coating chemistry. Even today they still accur over 40% of world production of synthetic coating resins. The huge success of alkyd resins can be attributed–in short–to an ideal combination of polyester and oil properties. The polyester component is responsible for physical (surface) drying and weather resistance (gloss retention, freedom from yellowing, etc). The oil component is important for the suppleness of the films (internal plasticization) and the suppleness of the films (internal plasticization) and all for the capability of oxidative crosslinking.

The strength of alkyd resins, such as self curing at room temperature as one component system provides very broad compatibility and solubility spectrum, virtually unlimited variability of properties by appropriate choice of raw material and synthetic condition, good pigment wetting, attractive flow properties leading to good spreadability of paints and relatively low cost.[2] The oil type selected for the production of usually alkyds has a profound effect on the properties of the finished alkyd. The presence of fragments derived from unsaturated fatty acids in the polymer structure gives them the ability to cure solubility chemically in the solvents used to manufacture varnishes. The ability to blend with other film-forming substance alkyd resins is cured due to intermolecular reaction of unsaturated bonds contained in the fatty acid chains and hydroxyl groups derived from polyols under the influence of oxidative polymerization initiators. The chain polymerization processes occur in alkyd resins to yield cross linking intermolecular bonds C-C and C-O-C.[3-4] However, the high numbers of unsaturated bonds in the fatty acid chains cause that not all unsaturated bonds react in the alkyd curing process. The presence of surplus unsaturated bonds in the cured coating leads to its yellowing following oxidation after exposure to atmospheric oxygen.. The coating chemistry generally classifies alkyd resins on the basis of their oil content or their fatty acid content calculated as triglyceride content, type of oil or fatty acid (linseed oil alkyd, soybean oil alkyd, etc) classification according to the oil content (triglyceride content). The resin is based on the following nomenclature as (1) less than 40% oil: short oil alkyd, (2) 40–60% oil: medium oil alkyd, (3) over 60 to 70% oil: long oil alkyd, and (4) over 70-85% oil: very long oil alkyd.

Long oil alkyd always dry by oxidation, and their high oil content provides good flow, high flexibility and easy manual processing. But also they lead to relatively slow drying, if conjugate oils or acids are used in the resin synthesis. Faster drying long oil alkyd resins are produced based on soybean oil used as sole film former for decorator paint.[2] Polyester amide and alkyd resins[5] have applications in different fields such as painting, coating, adhesives and binders for composites. The vegetable oils and other green renewable raw materials are common sources used in the organic coating industry especially for the synthesis of alkyd resin in preference to petroleum products due to increased worldwide awareness of environmental concerns.[6] Alkyd resins have acquired great importance because of their economy, availability of raw materials, biodegradability, durability, flexibility, good adhesion and ease of application.[7]

The traditional oils such as soybean[8] oil, linseed oil[9], sunflower oil[10] and coconut oil[11] are used in the synthesis of alkyd resin. This paper describes the synthesis of alkyd resins which are based on the new renewable raw material catalyst zirconium octoate (zirconium 2-ethyl hexanoate) as a new catalyst which act as base-catalyzed alcoholysis of soybean oil. The zirconium octoate in alcoholysis reaction prevent oxidation of oil so the formation of monoglyceride by using zirconium octoate as catalyst in this synthesis useful for the color of monoglyceride. In the present work, the physico-chemical and film performance properties of the synthesized alkyd resins were studied and compared with commercial resins.

2. MATERIALS AND METHOTDS

2.1. Materials

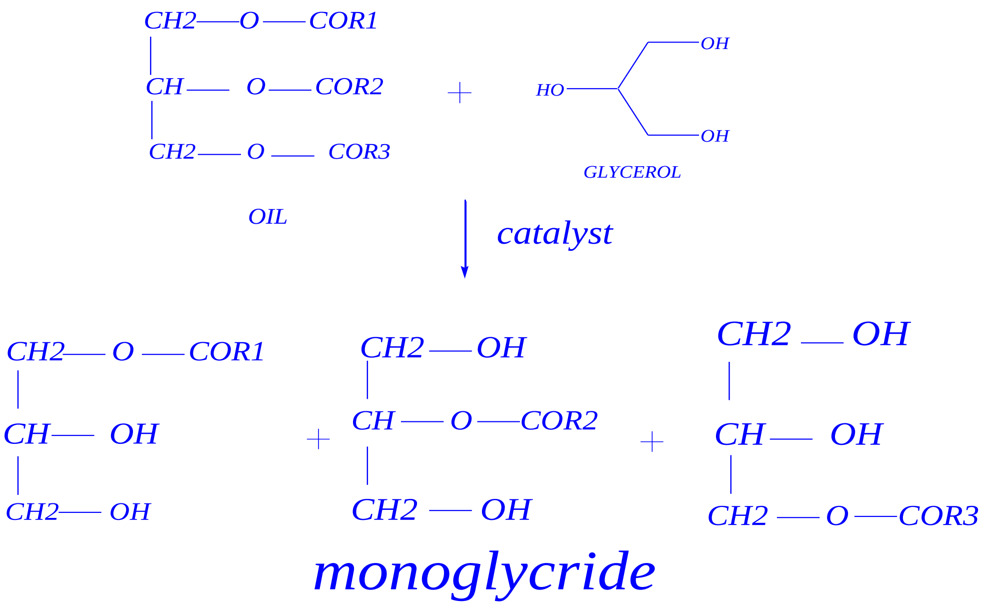
The soybean oil was provided from from oil technology company (purity 99.8%). Phthalic anhydride (99.9%), glycerin (99.8%), xylene (99.7%), methanol (99.6%), potassium hydroxide (100%), phenolpthaline (99.3%) were obtained from the Elgomhoria company. Lithium hydroxide (98.8%) was received from Dr Shahin chemicals, and cobalt octoate (99.8%), zirconium octoate (18% in mineral spirit), mineral spirit (99.5%) were purchased from a trade company.

2.2. Methods

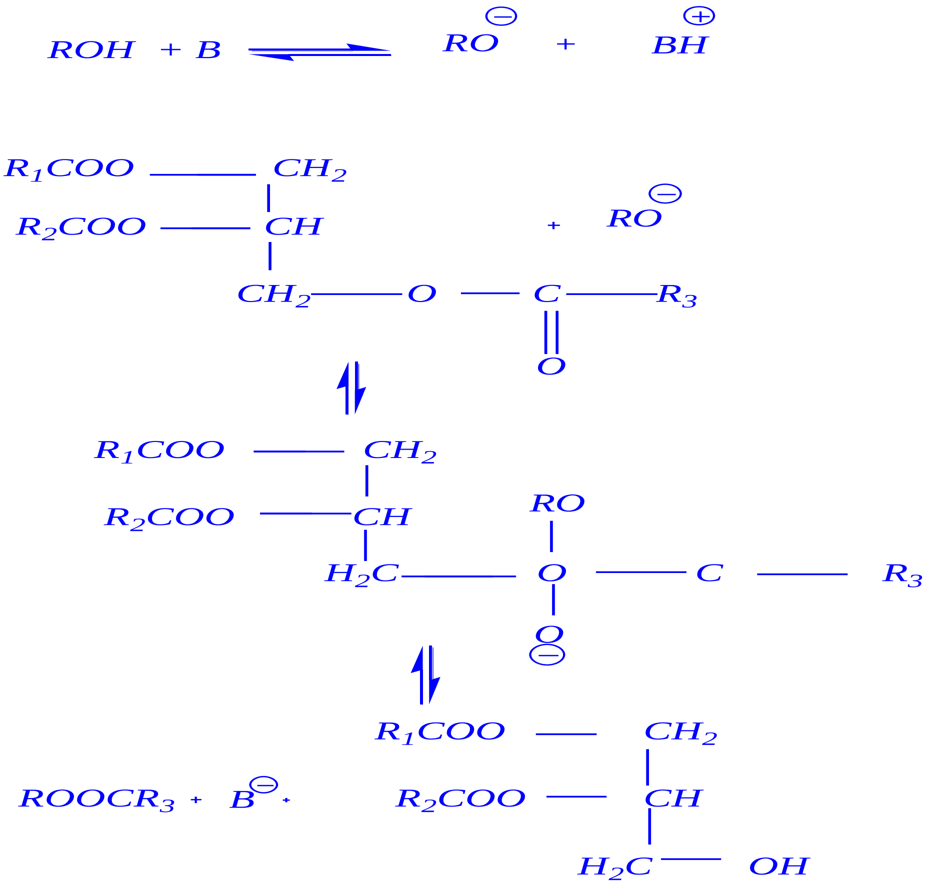
2.2.1. Alkyd resin synthesis

Alkyd resins were synthesized using monoglyceride fusion technique,[12] for this reason soybean oil, glycerin and lithium hydroxide (as catalyst) were charged into a four neck round bottom 1000 ml flask equipped with a mechanical stirrer, condenser and thermometer. The temperature was raised by slow heating to 290-300°C. The monoglyceride is formed by the alcoholysis process as seen in Scheme 1. The mechanism of the base-catalyzed alcoholysis of soybean oil for monoglyceride formation is depicted in Scheme 2.[13-14] The completion of monoglyceride process was monitored by testing the solubility of one volume of sample dissolve with two volume of methanol to give clear solution where the triglyceride can not dissolve in methanol but monoglyceride can dissolve in methanol. Then the reaction mixture was cooled to 180°C and phthalic anhydride was added the monoglyceride mixture. Then, the temperature was raised to 240-250°C and maintained at this range. The reaction was monitored by periodic determination of acid value (AV) of the mixture to desired number (10-14) mg KOH/g of the resin. The alkyd resin synthesis is shown in Scheme 3. The constituents of two resins along with some necessary characteristics are shown in Table 1.

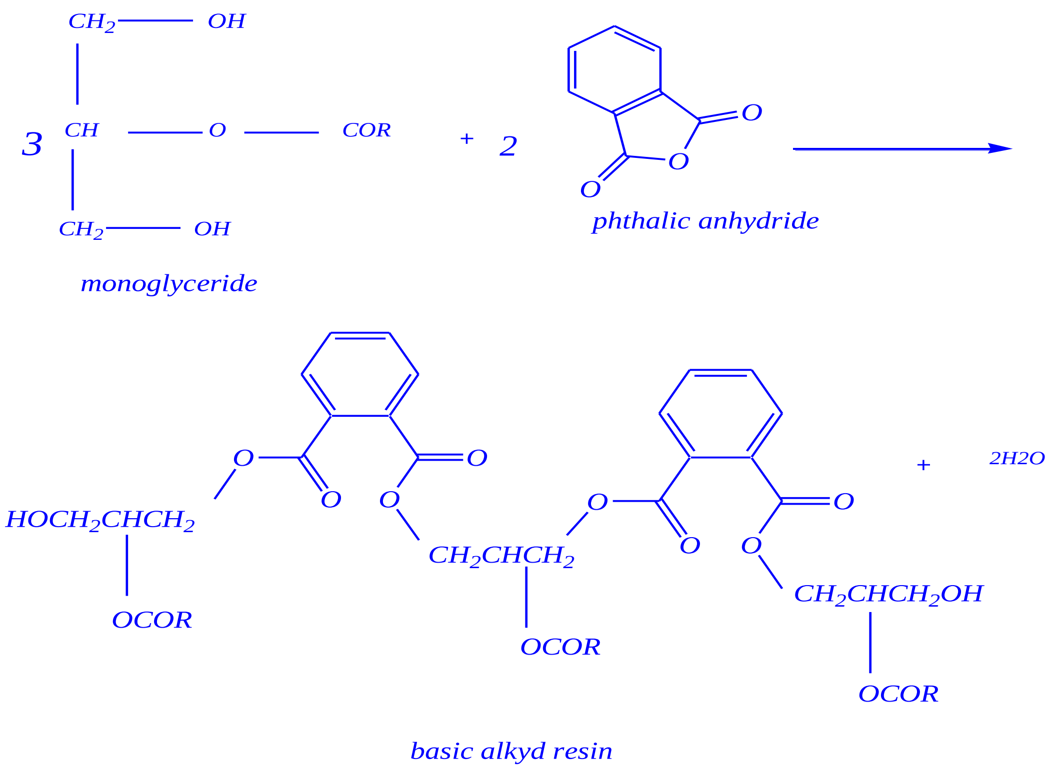
This process was repeated with zirconium octoate as catalyst but the temperature used in the preparation of monoglyceride was 290-300°C, and there was not nitrogen gas inlet. There was not nitrogen gas inlet. But nitrogen gas was used only in the stage of addition of ophthalmic anhydride to aid removal of water from reaction. In case of using lithium hydroxide as catalyst, nitrogen gas inlet was used in all stages of reaction.



Scheme 1. Transesterification of vegetable oil by glycerin for synthesizing alkyd resin.



Scheme 2. The base–catalyzed mechanism of alcoholysis reaction of vegetable oil.



Scheme 3. The synthesis of alkyd resin.

Table 1. The constituents of alkyd resins

Raw material (W %)	**Alkyd resin A**	**Alkyd resin B**
Soybean oil	54.9	54.9
Glycerin	16.22	16.22
Phthalic anhydrid	26.63	26.63
Lithium hydroxide	-	0.00816
Zirconium Octoate 18%	0.199	-
Xylene	0.02	0.02
Properties		
Acid value (100% solid) mg KOH/g	14	14
Solid content (%)	98	98
Viscosity (55% in WS) (cpoise)	2500	2900

2.2.2. The preparation of coating films

In order to study drying time, hardness, gloss and chemical resistance, two alkyd resins were applied onto cleand glass plates of 100 mmx100 mm x 3mm. The application was confirmed by applicator with slot width of 120 µm. The sample was prepared at 55% solution of each blend in the described solvent system with drying catalyst in the following amount (100 gm of resin dissolved in mineral spirit (cobalt octoate, zirconium octoate). Adhesion, mechanical were carried out on coated steel substrate. The cleand steel plates were used for this purpose. All coated plates were kept under stander conditions.

2.3. Characterization

2.3.1. The drying time test

The drying time was determined by "set-to-touch" and " tack-free" stages at regular interval of time. The test was confirmed according to ASTM D 1640(1995).

2.3.2. The hardness test

Two resins were applied on glass plates and were allowed to dry for one week of application. The test was confirmed according to ASTM D 4366(1997).

2.3.3. The adhesion test

The cross-hatch adhesion test was performed on the coated steel plates after one week of application. The test was confirmed according to ASTM D 3359(1997).

2.3.4. The flexibility test

The flexibility of the dried films was evaluated using the mandrel test according to ASTM D 1737. The coated steel film after a week of application was placed over the 118 in manderal with the uncoated side in contact with mandrel, and was bent 180 degree around it. The bended plate was examined visually for cracks or loss of adhesion. If the film passed through in mandrel then it was accepted to pass the flexibility test.

2.3.5. The impact resistance test

The impact resistance was measured by falling weight impact procedure according to ASTM D 2794. The test was accomplished on the coated steel plates after a week of film application.

2.3.6. The gloss test

The test was confirmed according to ASTM D 523 (1989). The sixty-degree gloss reading was taken on each of the films after the application in white lacquer.

2.3.7. The chemical resistance test

The chemical resistance test was accomplished according to ASTM D 1647(1996), D870(1997) and D1308(1998) on coated glass and steel plates after a week from the application. Alkali and acid resistance tests were accomplished on glass substrate immersed vertically in separate beakers containing distilled water, dilute HCl (10%), aqueous NaCl (10%) and KOH (4N) solutions at room temperature. The samples checked by eye. The appearance of the film at regular intervals within 1 day became changes.

2.3.8. The FT-IR and H^1-NMR analysis

The structure of two resin were confirmed according to the FT-IR and H^1-NMR spectra for resin at 500 MHz NMR spectrometer using $CDCl_3$ as the deuterated solvent.

3. RESULT AND DISCUSSION

3.1. The synthesis of alkyd resin

The alkyd resins were synthesized using lithium hydroxide and zirconium 2-ethylhexaneoate by alcoholysis process where soybean oil undergoes transesterification when heated with glycerol at 250 °C in case of lithium hydroxide as catalyst. Also, the alkyd resins were synthesized with nitrogen gas inlet until monoglyceride forms in case of the using of zirconium octoate.[13 -14] The soybean oil undergoes transformation to the monoglyceride by heating at temperature 290-300°C without any further oxidation and there was not nitrogen gas inlet. Then esterification was carried out with addition of ophthalmic anhydride. The nitrogen gas inlet was used as inert blanket when catalyst was lithium hydroxide to prevent the oxidation of oil. The nitrogen gas inlet was used in the second stage with zirconium octoate with addition of phthalic anhydride which facilitates the removal of water produced during mm condensation reaction. The reaction was controlled by measuring acid value at different intervals of time. The reaction was stopped as soon as the desired level of acid value was attained.

3.2. The structural analysis of the alkyd resins (A, B)

The FT-IR spectra of alkyd resins (A, B) are shown in Figures 1 and 2, respectively. These spectra indicate indicate the presence of important linkage of ester group, olefinic double bonds and other characteristic peaks. Characteristic peaks in FT-IR spectra of alkyd resins (A, B) are listed in Table 2.

Table 2. Characteristic peaks in FT-IR spectra of alkyd resin (A, B)

Peaks of resin A (cm^{-1})	Peaks of resin B (cm^{-1})	Functional groups
3472.55	3514.28	O-H stretching vibration
3008.8	3007.27	Olefinic C-H stretching vibration
2925.65 2854.38	2925.77 2857.13	C-H aliphatic stretching vibration
1735.1	1737.14	C=O stretching frequency of ester
1599.45 1580.28	1590.97	C=C stretching frequency of alkene an aromatic band
1489.18 1377.7	1455.8 1373.16	Symmetric and asymmetric bending of methyl groups
1280.77 1041.64	1275.5 1071.89	C-O-C stretching vibrations attached with aliphatic and aromatic moiety
742.65 705.98	740.84 570.33	Out of plane aromatic C-H bending vibration

For alkyd resin (A), the peak for C=O appears at 1735 cm^{-1} in case of synthesized resin. The peak at 3472 cm^{-1} indicates the presence of hydroxyl group. For alkyd resin (B), the polyesterification reaction is confirmed by FT-IR analysis and C=O observed at 1737 cm^{-1}. The peak at 3514 indicate the presence of O-H group, the peak at 1590 cm^{-1} indicates C=C stretching for unsaturation of fatty acids and aromatics.

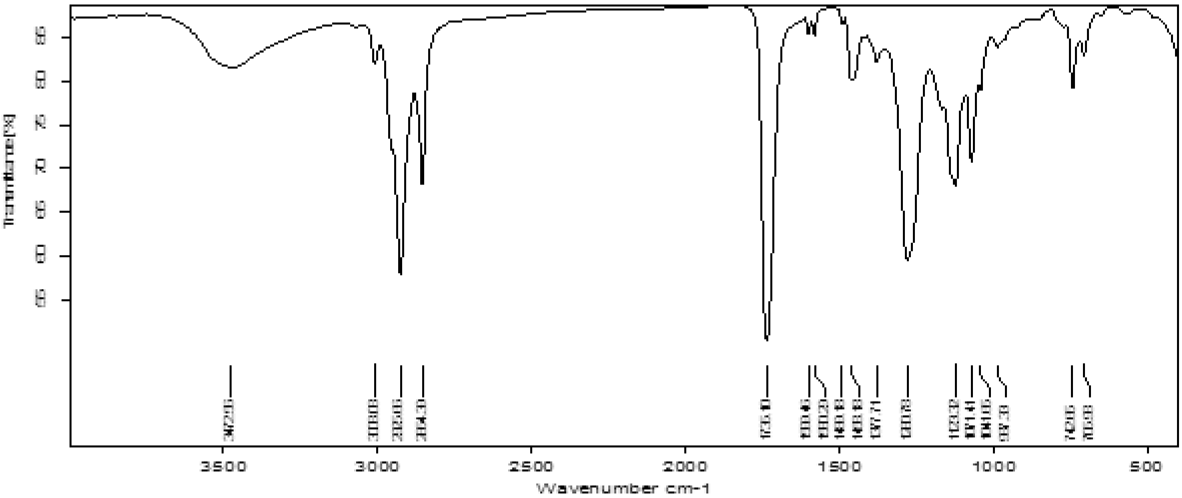


Figure 1. FT-IR spectra of alkyd resin (A) using Lithium hydroxide as catalyst.

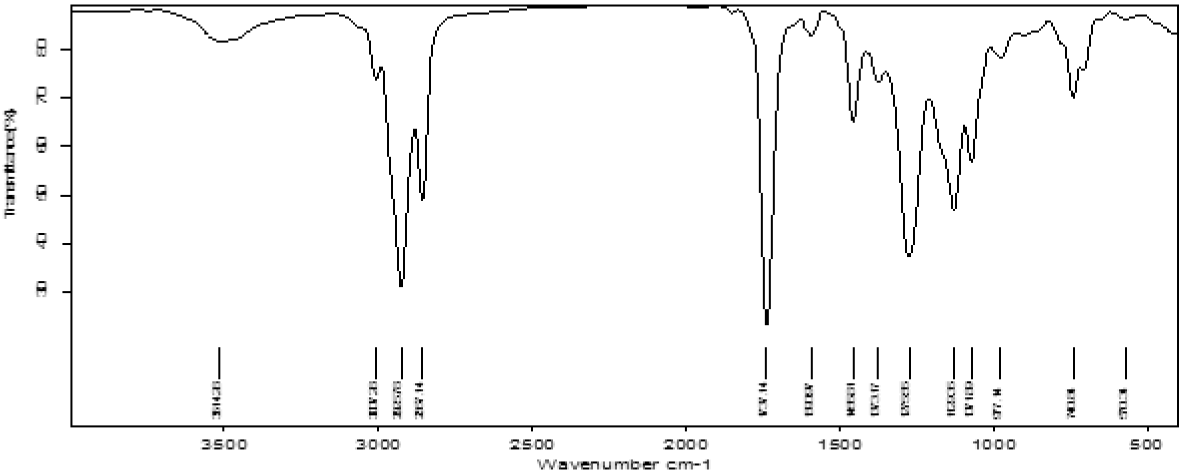


Figure 2. FT-IR spectra of alkyd resin (B) using zirconium 2-ethylhexanoate as catalyst
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H^1-NMR spectra of the alkyd resin A using lithium hydroxide (LiOH) as catalyst is shown in Figures 3. Peaks appeared at δ 0.96 ppm for the protons of terminal methyl groups of fatty acids was confirmed by this peak. The peaks next to that at δ 1.35 ppm are due to protons of all -CH_2 present in the chain of fatty acids. The peak at δ 5.42 ppm resonance due to the unsaturated carbon (olefinic hydrogen in the fatty acid chain). The proton of aromatic ring and xylene solvent used to dissolve resin can be depicted by peaks at the rang δ 7.00-7.78 ppm. The peaks appeared at δ 6.95-6.97 ppm for –CH present in glycerol molecule linkage to oxygen of the ester group. This may be due to the presence of anhydride groups which results in deshielding effect. The peaks appeared at δ 3.45-3.9 ppm for -CH_2 present in glycerol moiety attached to -OH group in the resin. The peaks appeared at δ 4.23-4-65 ppm for -CH_2 present in glycerol moiety attached (phthalic moiety). Peaks appeared at δ 2.3-2.4 ppm for -CH_3 attached to aromatic ring this due to xylene solvent present in sample resin. H^1-NMR analysis for resin B which the zirconium 2-ethylhexanoate used as catalyst for preparation the alkyd resin are shown in Figure 4. The proton of terminal methyl groups of fatty acids was confirmed by the peak δ 1.02 ppm. The peak next to that at δ 1.40 ppm are due to protons of all –CH_2 present in the fatty acid chain. The peak at δ 5.48 ppm are due to the unsaturated carbon (olefinic hydrogen in the fatty acid chain). The proton of aromatic ring of phthalic moiety and proton of aromatic ring of xylene moiety at the range δ 7.15-7.83 ppm. The peaks appeared at δ 4.26-4.70 ppm for –CH_2 present in glycerol moiety attached to (phthalic moiety). The peak appearad at δ 1.72 ppm are depicted to -CH_2 group attached to ester group of zirconium 2-ethylhexanoate catalyst. The peaks appearad at the range δ 2.32-2.44 ppm for -CH_3 attached to aromatic ring this due to xylene solvent present in sample resin. The peaks appearad at δ 7.05-7.08 ppm fo -CH present in glycerol molecule linkage to oxygen of the ester group. This may be due to the presence of anhydride groups which results in deshielding effect. The peaks appearad at δ 2.68-2.91 ppm for -CH_2 present in glycerol moiety attached to -OH group in the resin.

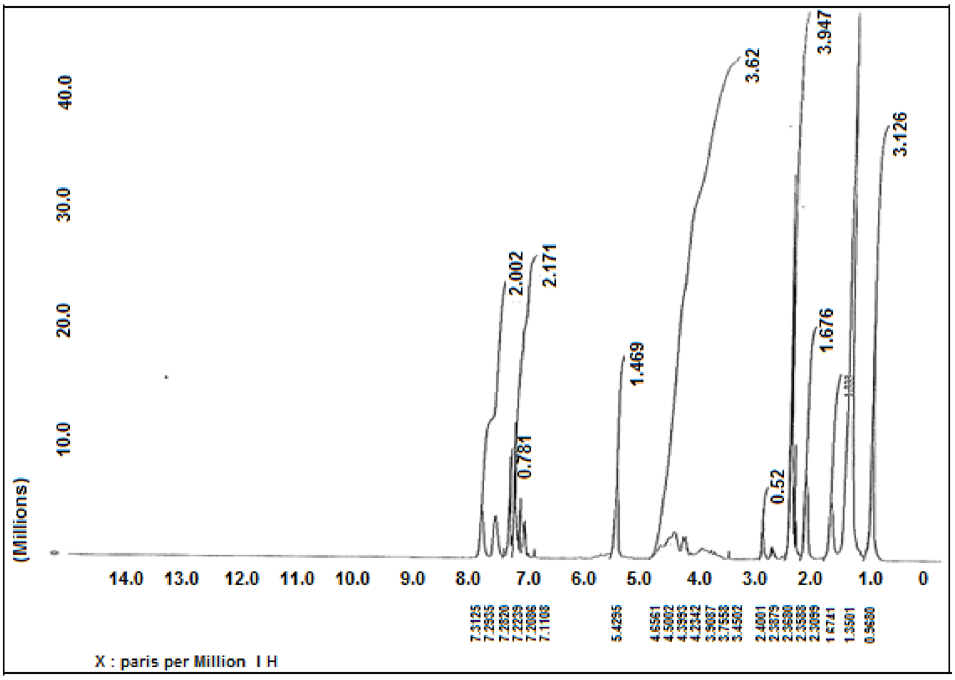

Figure 3. The H^1-NMR spectra of alkyd resin A using lithium hydroxide (LiOH) as catalyst.

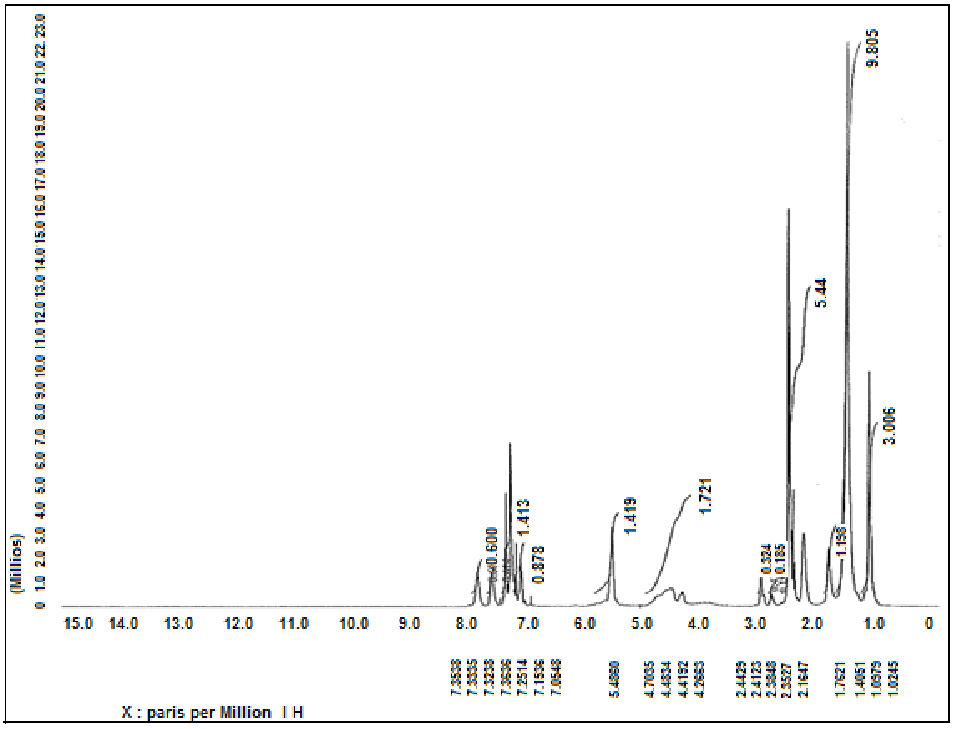

Figure 4. The H^1-NMR spectra of alkyd resin B using zirconium 2-ethylhexanoate as catalyst.

3.3. The drying time for resins (A, B)

Table 3 describes the time required to two resin dried where the first is set-to-touch and the hard drying of resin was tack free time. The alkyd resin film driers by auto-oxidation process.[23] due to intake of oxygen from atmosphere mechanistic studies of autoxidation drying process of coating based on alkyd resin have concentrated on methylene interrupted fatty acids[24], but there are many other theortical and empirical findings that are valid for other compounds .it is likely that a carbonyl group kinetically facilitates insertion of a transition metal ion into α-carbon-carbon bond.[25] The hydrogen atoms attached to carbon atoms in α-position of carbonyl group are more active(acidic)compared to ordinary alkyl hydrogen and similar that hydrogen atoms attached to ester group in alkyd resin , these hydrogen atoms are deprotonated by zirconium octoate salt, providing an enolate anion (Michael donor), the enolate anion then reacts an addition to olefin of the fatty acids emerged during the oxidative crosslinking of alkyd resin by Russell mechanism.[26-27] All these interesting possibilities speed up the network formation and result in lower drying times.

3.4. The adhesion test for resin (A, B)

Results are given in Table 3. The results showed a desired adhesion for resins (A, B) where two resin prepared from the same oil (soybean oil) and glycerin which give the same polyester component which responsible for adhesion.

Table 3. Adhesion and hardness test results of alkyd resins

	Set-to-touch (min)	Tack free time (min)	Hardness (s)	Adhesion %
Resin A	75	360	14	100
Resin B	80	350	16	100

3.5. The hardness

Results are given in Table 3. The results show the hardness increases by using the zirconium catalyst than toward the use of lithium hydroxide catalyst in the synthesis of resin. This indicates when alkyd resin prepared using zirconium catalyst and zirconium octoate used in drying resin with octoate cobalt, the hardness of dried film increases with small amount of hydrocarbone resin in varnish industry. The film hardness depends on crosslinking density of the surface of the film, but presence of stable and rigid aromatic moiety in the backbone chain of phthalic anhydride – based film also showed the property zirconium octoate as drier which made resin B gave good hardness than resin A. But the two values of hardness are close to each others. [21-22]

3.6. The flexibility

Table 4 gives the flexibility test results. Two samples passed the test and no cracking or peeling was observed. This may be due to the oil content in the prepared alkyd resin

Table 4. Flexibility, impact resistance, gloss test results of alkyd resins

	Flexibility	Impact resistance cm	Gloss 60°,%
Resin A	passed	125	86
Resin B	passed	135	87

3.7. The impact resistance

The impact resistance results are given in Table 4. Two resin prepared using lithium hydroxide and zirconium 2-ethylhexanoate catalyst dried films show significant improvements in impact resistance. The resin prepared from zirconium catalyst gives a good impact resistance due to the zirconium element.

3.8. The gloss

Results of gloss test are given in Table 4. The gloss values of resins prepared from zirconium catalyst and lithium hydroxide is like approximately each other, which means the two resin contains the same percentage of oil and polyester component responsible for gloss retention.

3.9. The chemical resistance

Chemical resistance of dried film are given in Table 5. The resin A and resin B was good resistance to distilled water this due to low hydroxyl value present in alkyd resin and more cross-linked network results and two resin completely unaffected with NaCl 10% for the same reason. Poor alkali resistance of alkyd resin is due to the presence of alkali hydrolysable ester linkages and the alkyd resin containing free acid groups which react with alkali. Two alkyd resin unaffected with HCl 10% this due to two resin contain acid number and ester linkages poor affected by HCl 10%. The poor rsistivity to alkali is probably due to hydrolsable ester group present in the two resin.[20]

Table 5. Chemical resistance test results of alkyd resins

	Distilled water	**NaCl (10%)**	**KOH (4 N)**	**HCl (10%)**
Resin A	Completely unaffected	Completely unaffected	Completely affected	Unaffected
Resin B	Completely unaffected	Completely unaffected	Completely affected	Unaffected

3.10. The yellowing resistance

The tendency for alkyd based coatings to yellowing is a common concern all over the organic coatings industry.[15-16] The oils containing linolenic acid are subject to discoloration because it is known this acid is the main cause of discoloration.[17–18] The soybean oil contains 54% linoleic acid, therefore, soybean oil is good yellowing resistance where soybean oil is widely used around world. The aim of this work the tendency of lowering yellowing across the preparation of monoglyceride using zirconium octoate to prevent autoxidation of oil and production of alkyd resin transparent after application on glass blend. The alkyd resin prepared from zirconium catalyst when applied in white lacqure was given good color and high yellowing resistance than white lacqure prepared from commercial resin.[19]

3.11. The acid value with time

For the polyesterification reaction , the acid value change with time are shown in Figures 5 and 6.

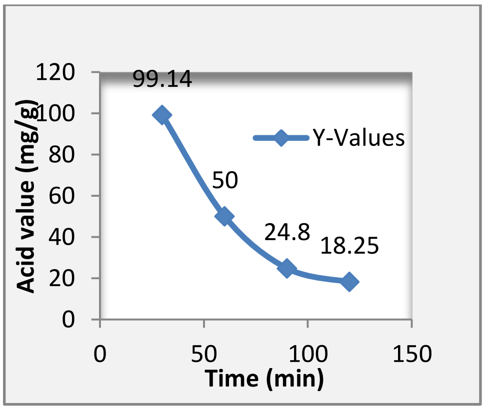

Figure 5. Acid value determined using zirconium octoate as catalyst.

The acid value and hydroxyl number are important parameters. The hydroxyl and carboxylic group concentration is also quite important parameters. For air drying alkyds, the concentration of these groups affects their drying properties. Set-to-touch drying time of resin A took lower time than resin B, but resin B was prepared from zirconium -2- ethylhexanoate which gave tack free time in drying process lower than resin A according to Table 3.

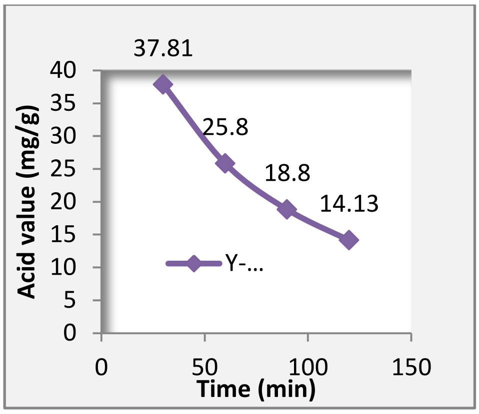

Figure 6. Acid value determined using LiOH as catalyst.

Of course this is not the only parameter that determines the properties of the resins. Many other factors also affect their properties. In this work although acid value of resin B takes more time to adjust like resin A. Because the resin A is prepared from strong base which reacted with carboxylic groups and lowered acidity, but the drying time and yellowing resistance finally of resin prepared from zirconium octoate is better than resin prepared from lithium hydroxide .

4. CONCLUSIONS

The results obtained in the present work showed the ability of zirconium octoate salt to synthesized the monoglyceride from soybean oil and glycerin by alcoholysis reaction and prevent the oxidation of oil at high temperature where the monoglceride formed in the absence of nitrogen gas inlet this is best result was obtained by this catalyst since the catalyst reduce the cost in the production alkyd resin and protected the reaction from oxidation which take place during the preparation of resin . The zirconium octoate salt can act as base-catalyzed transformation of triglyceride by glycerin to form monoglyceride under high temperature. The structure of alkyd resin was confrmed by FT-IR and H^1-NMR spectroscopy and comparable with the alkyd synthesized LiOH catalyst. The physico-chemical characteristics reffered to the resin prepared from zirconium octoate salt was good yellowing resistance when formulated in white lacqure. The other properties were good at drying time, gloss. The zirconium octoate catalyst gave the best results in yellowing processe since the alkyd resin prepared could resist the yellowing for along time compared resins prepared from other catalysts.

Conflict of interest

Authors declare that there is no a conflict of interest with any person, institute, and company, etc.

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