

# Synthesis And Characterization Of New Styrenated Alkyd Resin From Olive Oil As Binder For Surface Coating

Ruaa Jameel Kamel<sup>1\*</sup>, Farah Safi Khliwi<sup>2</sup>, Ammar Ali Hussein<sup>3</sup>, Karrar hazim Salem<sup>4</sup>, Mohamed Ali Mutar<sup>5</sup>

<sup>1</sup>College of Pharmacy, University of Al-Qadisiyah, Iraq.

<sup>2</sup>Department of Chemistry, College of Education, University of Al-Qadisiyah, Iraq.

<sup>3</sup>Najaf Education Directorate, Iraq

<sup>4</sup>Pharmacy Department, Al-Mustaqbal University College, 51001 Hillah, Babil, Iraq

<sup>5</sup>Department of Chemistry, College of Scientific, University of Al-Qadisiyah, Iraq

\*Corresponding Author: Ruaa Jameel Kamel

<sup>1</sup>College of Pharmacy, University of Al-Qadisiyah, Iraq.

DOI: 10.47750/pnr.2022.13.S05.26

## Abstract

In the current review article, an effort has been made to emphasize the inner workings of alkyd resins, the earliest polymeric resin created from vegetable oils, in light of technological advancements that have occasionally been made to increase their practical utility. The thorough synthesis and use of several kinds of water-born alkyds were explained in order to lessen the use of organic solvents. To create one set of styrenated alkyds, the Styrene monomer was used to post-polymerize the alkyd at 5:5 ratio at 80 °C for 6 hours. 1 Standard techniques were used to define and assess the styrenated alkyds' physical and chemical characteristics, drying time, and chemical resistance. Each resin displayed favorable characteristics. Even without a dryer, the styrenated alkyds provided a quicker drying time<sup>2</sup>. The styrenated alkyds were resistant to alkali, in contrast to the unstyrenated alkyd, which is just resistant to conditions that are acidic, wet, or briny. The AAST's coatings The FTIR, HNMR, DSC, and TGA methods were used to confirm the structures of the changed resins that were obtained. The findings of the physico-mechanical tests demonstrated that the styrenated alkyds that were produced are suitable for a range of coating applications.

**Key word:** styrenated alkyds, coating, physical properties.

## INTRODUCTION:

The (ARs) with the lowest branching degree are polyesters synthesized from a dibasic acid, polyols, and oils.<sup>[1]</sup> The coatings industry has used these resins extensively.<sup>[2]</sup> The resins have excellent flexibility, adhesion, and high gloss.<sup>[3]</sup> However, because they are produced using volatile organic compounds (VOCs), which are harmful to humans, plants, and animals and contribute to global warming, they are not environmentally friendly. Numerous studies are being undertaken in the modern day to produce alkyd resin with the least amount of VOCs possible. In a previous work, (HAR)<sup>[4]</sup> or modified HAR were created to have a high solid content.<sup>[5]</sup> In a different investigation, VOC-free AR emulsions were created. Styrenated alkyd resin was used to create AR or HAR that had been treated with styrene monomers.<sup>[6]</sup>

To create styrene-alkyd resins in the shape of stars, AR can be modified using styrene (SSARs). A different source claims that polystyrene (PS) is strong, resistant to acids and bases, and has good optical clarity.<sup>[7]</sup> As a result, a synergy can be created by combining PS qualities with AR properties. According to several studies describing the creation of unsaturated modified with Styrene, the modification enhances the mechanical properties of unsaturated polyester (Young's modulus and tensile strength).<sup>[8, 9]</sup>

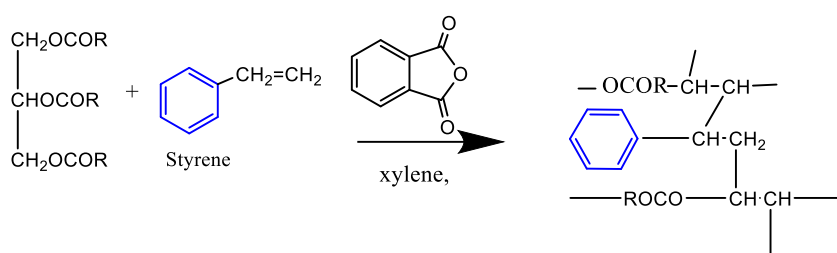
Alkyd has some benefits, such as good adhesion, film flexibility, color, gloss, and application over a wider temperature range, but it also has some disadvantages, such as its sensitivity to alkali due to the hydrolysis reaction that splits the ester linkages, which is a reaction that is very typical of esters. In addition, alkyd resin dries relatively slowly as compared to other synthetic resins. However, it can be altered through a number of chemical and physical processes, including co-polymerization, producing goods that could be used in a numerous applications. This is shown by the fact that it is very compatible with a variety of other polymers, such as acrylic, nitrocellulose, phenol, epoxy resin, etc., where the technical properties of both polymers are combined to generate goods with better attributes that are appropriate for a variety of end purposes.<sup>[10, 11]</sup>

The advancement of eco-friendly materials has attracted both consumer and industry interest, which has propelled the use of ecologically friendly using farm products used as a feedstock to make useful polymers Various renewable natural resources have been used in attempts throughout the years to create specialty compounds that are ecologically benign. [12-14]. Natural resources like plants and herbs are widely available and offer a variety of Biological feedstocks that may

be tailored to create various value-added commodities. [15,16] Polyester resin, also referred to as alkyd resin, is one of the earliest triglyceride oil-based polymers. [15-17] Since it is nearly impossible to conceive any product intended for long-term use without an organic coating applied to its surface, organic coatings account for a sizable portion of the polymer materials industry. These substances are used on a substrate primarily for their protecting and adorning qualities. Depending on the nature of the substrate and the circumstances of its use, the protective function includes creating a barrier against external agents such as fire and mechanical abrasion in addition to water, air, acids, alkalis, and organic liquids. Organic coatings' ornamental qualities can be seen in their color, transparency, gloss, texture, and combinations of these attributes. Polymer resins serve as a binder and are the primary constituent of organic coatings. [18]

## METHODS:

Alkyd formulation a flask with three necks equipped alongside Dean and Stark was used to create medium oil length RSO alkyd using the monoglyceride process as stated in an earlier report [19,20] while operating in an azeotropic and reflux environment. Alkyd was thinned, the proper thin films were created after adding a quantity of driers of the mixture were placed on glass panels and allowed to dry by air. Using ASTM procedures, the alkyd's physico-chemical and coating characteristics were assessed. Styrenation The alkyd resin underwent post-co-polymerization to produce the styrenated alkyds. A 250 ml quick-fit flask was used to draw and heat the alkyds under reflux for 8 hours (samples I through v) and 6 times as described in Table 2 in the presence of an initiator, potassium per sulfate, at 85°C in ratios of 4:4. Without using a dryer, the polymer was thinned and put in thin sheets to a glass panel. The resulting styrenated alkyds were identified and assessed for coating characteristics including drying and chemical resistance.



Scheme (1) preparation of oil modified ARs and styrenated alkyd reaction scheme

## RESULTS AND DISCUSSION

**Table 1;** Alkyd (Olive oil –short)

| Acidity | No. of soap | No. of iodide | Density | Viscosity |
|---------|-------------|---------------|---------|-----------|
| 6.6     | 194         | 92            | 0.9150  | 80 cp     |

According to the values listed in the table, the outcome is as follows: The quality of oil used to prepare alkyd resins can be determined by the oil's acidity value, which indicates the prevalence of rancidity. The length of the acid chain employed in the preparation is determined by it. Results from the olive oil suggested that it could be stored for a long time because the resin needed for preparation had a short chain. The saponification results also demonstrate the short chain length of the oil used to make alkyd resin. Due to the short acid chain, the value of the iodine number also shows the presence of modest amounts of unsaturation in the chain. Due to the short acid chain utilized, alkyd resin has a high density and high viscosity.

**Table 2;** Solubility of alkyd

| Acetone | Ethanol | Methanol | Xylene | Kerosene | Toluene | DMF | Benzens |
|---------|---------|----------|--------|----------|---------|-----|---------|
| +       | -       | +        | +      | +        | +       | +   | +       |

Alkyd have a tendency to be soluble in both polar and aprotic nonpolar solvents due to its Lewis behavior and hydrogen bonding..

**Table 3;** Chemical resistant of alkyd

| H <sub>2</sub> O | H <sub>2</sub> SO <sub>4</sub> | HCl | NaCl | KoH | THF |
|------------------|--------------------------------|-----|------|-----|-----|
| +                | -                              | -   | +    | +   | -   |

Although this organic solvent is non-polar., AR has good resistance to acids and is not dissolved in these solutions despite being resistant to water, salt, and basic solutions.

(-) Refer to in soluble alkyd resin (resistant)

(+)Refer to soluble alkyd resin (non - resistant)

styrenated alkyds risen (AAs)

**Table 4;** Value of physical properties of (AAs)

|                 | Viscosity      | Density | Drying | Volatile |
|-----------------|----------------|---------|--------|----------|
| AA <sub>s</sub> | More 20.000 cp | 0.823   | 7.30 h | 0.2250   |

According to the obtained results, the emulsion has good results for viscosity and density values, as well as volatility and dryness.

The presence of aromatic monomer structures in the (AAs composition,)s the oil's short chain and the quantity of double bonds all contribute to the substance's high viscosity. (AAs) Due to the short acid chain and the existence of a single monomer, density rises. Due to the fatty acid utilized in the manufacture of the alkyd and the presence of styrene.

Monomer in the resin composition, the volatility and dryness give these properties their value. When (AAs) have characteristics that fall between hydrophilic and hydrophobic.

**Table 6;** Solubility of (AAs)

| Solvent                         | AA <sub>s</sub> |
|---------------------------------|-----------------|
| Benzene                         | -               |
| DMSO                            | +               |
| THF                             | +               |
| CHCl <sub>3</sub>               | +               |
| CH <sub>2</sub> Cl <sub>2</sub> | +               |
| Acetone                         | +               |

Because of their Lewis behavior and hydrogen bonding, (AAs) have a tendency to be soluble in polar aprotic solvents and nonpolar solvents, with the exception of benzene.

**Table 7;** Chemical resistant of alkyd

| Solvent                        | AA <sub>s</sub> |
|--------------------------------|-----------------|
| H <sub>2</sub> O               | -               |
| HCl                            | -               |
| NaOH                           | +               |
| H <sub>2</sub> SO <sub>4</sub> | -               |

Because of their Lewis behavior and hydrogen bonding, (AAs) have a tendency to be soluble in polar aprotic solvents and nonpolar solvents, with the exception of benzene.

#### Corrosion Test.

| Sample          | Time  |
|-----------------|-------|
| AA <sub>s</sub> | 4 day |

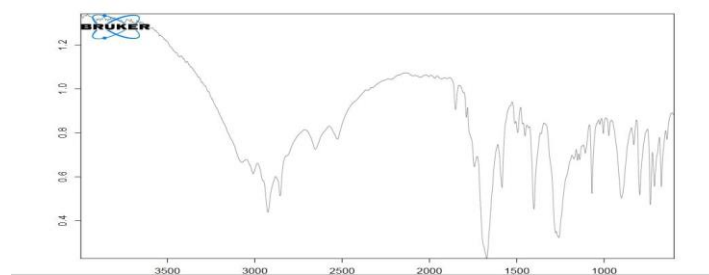
The most frequent and divisive testing for corrosion resistance are likely salt spray tests. Since in order to protect such substrates from corrosion, it is advantageous to comprehend how a certain system operates in both healthy and damaged coating films. This is because it is well known that salts like sodium chloride can induce fast corrosion for ferrous substrates. Nevertheless, they are well-known, and despite the challenges of reproducibility and the scarcity of information on long-term corrosion, they are incredibly useful as performance guides. Furthermore, it seems unlikely that they were thrown out. Some employees view them as impracticable due to the level of corrosion process acceleration they achieve and the lack of assurance regarding the degree of damage caused in some of the tests. As shown in Table 7, adding (alkyd) to the acrylic polymers' structural core has resulted in a coating that is greater salt spray and moisture resistance.

#### Resistance to abrasion

| Sample          | Abrasion |
|-----------------|----------|
| AA <sub>s</sub> | 700      |

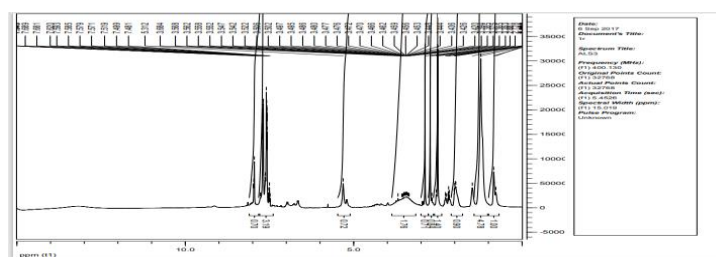
Is a sign of a coating's resilience to impacts, hardness, and durability. The test results reveal how much sand is needed to remove a particular coating thickness. The quantity of sand required to eliminate a coating layer of 1 mm thickness is determined by the results of the abrasion resistance test in Table (8).

The FTIR spectra of (AAs ) as shows at Figure (1) where absorption bond for (O—H acidic) in (3385cm<sup>-1</sup>), carbonyl group of COOH in (1744cm<sup>-1</sup>), (C=O) carbonyl group of RCOOR in (1720cm<sup>-1</sup>), (C—H) aliph. in (1380,1430cm<sup>-1</sup>), (C—O) RCOOR in (1188cm<sup>-1</sup>), (C—H) for methyl in (2890cm<sup>-1</sup>), (C—H)ar. in (3011cm<sup>-1</sup>), (C=C)ar. at (16205cm<sup>-1</sup>).



**Figure (1)** FTIR spectra of AAs (Alkyd styrene)

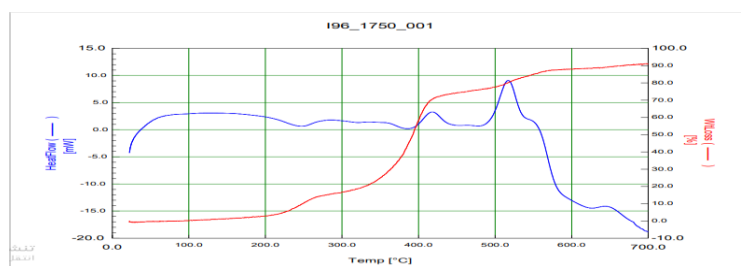
Figure (3) showed signals at ( $\delta=2.66-3.444\text{ppm}$ ) for (CH<sub>3</sub>), as well as signals at ( $\delta=3.448-3.470\text{ppm}$ ) for (CH<sub>2</sub>). A number of signals appearing at (3.495-3.547ppm) caused by (CH) protons a number of signals appearing at (3.495-3.547ppm) caused by (CH) protons. It shows a single for proton in RCOOH at ( $\delta=7.689\text{ppm}$ ).A single at (7.481-7.7585ppm) for H in aromatic ring.



**Figure (2)** NMR-H<sup>1</sup> spectra of (AAs)

**Thermal properties**

**Thermal gravimetric analysis (TGA) &DSC study**



**Table (9):** Thermal behavior data of Alkyd resins

| Alkyd resins               | TGA/°C         |                 |                | T <sub>50%</sub> | Residue % at 600°C | Char %at 700°C |
|----------------------------|----------------|-----------------|----------------|------------------|--------------------|----------------|
|                            | T <sub>i</sub> | T <sub>op</sub> | T <sub>f</sub> |                  |                    |                |
| <i>Styrene Alkyd-Short</i> | 150            | 280             | 500            | 370              | 5                  | 7              |

**Thermo Gravimetric Analysis (TGA) Study.**

Numerous temperature fluctuations in the bulk are examined as part of the thermo gravimetric analysis (TGA). It is frequently used to look for gradient temperatures, the amount of absorbed component, the proportion of inorganic and organic elements in a component, and the examination of solvent residues. The specimens are suspended from a temperature-programmer-controlled furnace using a responsive electronic scale. Two samples of the vest's thermal properties were gated by these emulsion acrylic copolymers using thermo gravimetric 10°C/min of heating during a TGA analysis in an Argon atmosphere. Results such as T<sub>i</sub>, T<sub>op</sub>, T<sub>f</sub>, T<sub>50%</sub>, percentage residue at 500°C, and the char yields shown in (Table 9) following treatment at 700°C.

**Table (10):** Displays in the differential thermal analysis the degree of glass transition, melting point, and degree of crystallization

| Sample                     | T <sub>g</sub> (°C) | T <sub>m</sub> (°C) | TC(°C) |
|----------------------------|---------------------|---------------------|--------|
| <i>Styrene Alkyd-Short</i> | 50                  | 550                 | 250    |

**Study on Differential Scanning Calorimeters (DSC)**

Scanning for comparability Calorimetry is a technique for conducting thermal analysis that examines how temperature affects a component's heat capacity (Cp). In addition to salt aeration being seen in the heat flow as a result of changes in the sample's heat flow, heat is applied to a known mass sample or chilled. This makes it possible for changes like the

transition to molten glass (T<sub>g</sub>) and the (T<sub>c</sub>) to be revealed by the degree of crystallization (T<sub>c</sub>) (15). The mixture's (T<sub>g</sub>) value (50°C) is displayed in the test results for the (AAs) polymer in table(10), along with the temperature flow and the pace at which a specimen absorbs energy to reach the m.p (T<sub>m</sub>) at 550°C.

## CONCLUSIONS

According to the results, none of the acrylic alkyd copolymers' that were employed to make the emulsion exhibited a non-Newtonian pseudo plastic form. The shear rate, viscosity, and compliance of the acrylic acid were all very high. The polymer containing a acrylic alkyd monomer in the mix has a good thermal stability. For hybrid binders with larger resin concentrations, salt spray analysis indicates improved corrosion-resistance. The physical properties are sensitive to changes in temperature for thermal treatment because of the chemical reaction that occurs through the reactive groups which are combined with the main chain of polymers. Better these are achieved for copolymers the higher the thermal treatment temperature. A hybrid acrylic emulsion produced by polymerization results in less volatile organic compound (VOC) than conventional systems. It illustrates how we can enhance a hybrid system's qualities by incorporating two components, and how the other aspects are unaffected when the quality of one component rises. In coatings where corrosion resistant paints are required, these resins could be used. Resistance to various chemicals as well as abrasion, corrosion, and both.

## REFERENCE

1. Rämänen, P.; Pitkanen, P.; Jamsa, S.; Maunu, S. L. *J. Polym. Environ.* 2012, 20, 950.
2. Nikolic, M.; Sanadi, A. R.; Löf, D.; Barsberg, S. T. *J. Mater. Sci.* 2017, 52, 7158.
3. Christensen, P. A.; Egerton, T. A.; Lawson, E. J. *J. Mater. Sci.* 2002, 37, 3667.
4. Kanai, T.; Mahato, T. K.; Kumar, D. *Prog. Org. Coat.* 2007, 58, 259.
5. Bat, E.; Gündüz, G.; Kısakürek, D.; Akhmedov, J. M. *Prog. Org. Coat.* 2006, 55, 330.
6. Murillo, E. A.; López, B. L. *Polímeros.* 2016, 26, 343.
7. Odian, G. *Principles of Polymerization.* Vol. 4, Chapter 3. 4nd ed.; John Wiley & Sons: New Jersey, 2004. p. 303.
8. Costa, C. S. M. F.; Fonseca, A. C.; Moniz, J.; Godinho, M.; Coelho, J. F. J.; Serra, A. C. *Express Polym. Lett.* 2017, 11, 885.
9. Jel\_c, Ž.; Ranogajec, F. *Polimery.* 2010, 31, 113.
10. Wang C, Lin G, Pae J, Jones FN, Ye H, Shen W (2000). Novel synthesis of carboxy-functional soybean acrylic-alkyd resins for water-reducible coatings. *J. Coating Technol.* 72: p. 904.
11. Uzoh, C.F., Onukwuli, O.D., Odera, R.S. and Okey – Onyesolu, C.F. (2013). Synthesis and characterization of palm oil based air drying alkyd resin for surface coating, *Research Journal in Engineering and Applied Science*, 2(3), 187 – 191.
12. Sharmin, E., et al., *Industrial Crops and Products*, 2015, 26: p. 215-229.
13. Samarth, NB., and Mahanwar, PA., *Open J. Organic Polym. Mater.*, 2015, 5: pp: 1-22.
14. Ahamad, S., Ahmad, SA. and Hasnat, A., *Chem. Sci. Trans.*, 2015, 4: pp: 1047-1053.
15. Islam, MR., Beg, MDH. and Jamari, SS., *J. Appl. Polym. Sci.*, 2014, 131: pp: 40787-40799.
16. Ahamad, S., et al., *Orient. J. Chem.* 2015, 31: pp: 1169-1173.
17. Guner, FS. Yagci, Y. and Erciyes, AT., *Progress polym. Sci.*, 2006, 31: pp: 633-670.
18. Alam, M., et al., *Arabian J. Chem.* 2014, 7: pp: 479-479.
19. Ikhuoria EU, Aigbodion AI (2005). Studies in the quality of rubber seed oil-modified alkyd resin prepared with phthalic acid and adipic acid. *Int. J. Chem.* 15(1): 71-76.
20. Ikhuoria EU, Aigbodion AI (2006). Determination of Solution Viscosity Characteristics of Rubber Seed Oil Based Alkyds Resins. *J. Appl. Polym. Sci.* 101: 3073-3075.