Short Alkyd Resin Synthesis and Characterization Based on Sesamum Indicum Seed Oil as Binder for Coating Industry

Abstract

Alkyd resin of 40 % oil length was synthesized from the polyesterification reaction of glycerol, pthalic anhydride and sesame seed oil. Physicochemical properties such as iodine value, saponification value, density, moisture absorption, acid value and viscosity were determined to be 70.2 gI2/100g, 227.5 mgKOH/100g, 0.953 g/cm3, 0.22 %, 9.23 KOH/g and 123.22 m.Pa.s respectively for the sesamum indicum seed oil modified alkyd resin (SISOMAR). Differential scanning calorimetry and thermogravimetric analysis were employed for the characterization of the alkyd resin. The glass transition (T_g) value of the 40% alkyd resin was 34.99 °C, initial degradation temperature (T_i), final degradation temperature (T_f) were 300 °C and > 500 °C respectively. It was identified that the SISOMAR could meet with temperature resistance and mechanical requirements to serve as a potential binder for the coating industry.

Keywords: alkyd resin, Sesame, alcoholysis, polyesterification

1 Introduction

One of the oldest oil crops grown for human use and production is sesame (Sesamum indicum L.), which along with soybean, peanuts, and soybean oil are referred to as China's four main oil crops [1]. Sesame is a widespread cultivated crop that was first seen in Pakistani historical sites [2]. It is sold in places like Malaysia, China, and India. More than 5000 years ago, the Chinese began using sesame seeds [3]. Sesame is mostly produced in India, Sudan, Myanmar, China, and Tanzania on a global scale. Sesame is a remarkably adaptable plant with numerous uses in addition to those listed above. For instance, copy paper can be made from hot-pressed sesame oil. High-quality ink may be created using the vapors produced by burning sesame oil. Industry can use sesame to create lubricating soap[4]. Alkyd resins, which are essentially polyesters, are the products of the reaction between polyhydric alcohols and polybasic acid. With the addition of monobasic fatty acids or triglyceride oil, the reaction is essentially a polycondensation [5]. In the surface coating industry, drying and semi-drying oils like linseed, castor, soybean, and tall oil have been utilized as benchmarks for alkyd manufacturing [6].

Paints can be thought of as a colloidal mixture of chemical components that, when applied to a surface in a thin coat, form a layer that is dense, uniform, and adhering. They are frequently utilized in our daily lives for decorative purposes and to shield surfaces from environmental influences like UV rays, toxic chemicals, and mechanical stressful situations [7].

Because of economic development and expansion in the coating industry, there has been an increase in demand for a substitute in alkyd resin production. In order to produce alkyd resins with qualities similar to those used traditionally, it is therefore necessary to look into alternative sources of vegetable oils [8]. According to [9], soybean, castor, and linseed oils are frequently imported, pricey, and unavailable locally.

Qualitative structural analysis of the alkyd polymer has been carried out by employing differential scanning calorimetry, and thermogravimetric analysis in other to ascertain for its thermal stability and polymeric properties such as glass transition, crystallization temperature and melting point were investigated.
The iodine, saponification and moisture absorption tests will individually highlight the suitability of the alkyd resin in coating formulation. The iodine value will give an idea on the drying properties of the alkyd resin, the saponification value will highlight the extent of ester linkages inherent in the seed oil whilst, the moisture absorption test will serve as a blueprint in the utilization in the coating industry as it reflects the extent of resistance to blistering [5].

Pic 1. *Sesame Indicum*: Plant **(a)**, Seeds **(b)**

2 Methodology

2.1. Materials

In Adamawa State, Nigeria, sesame seeds were purchased from a local trader at Jimetta market. The equipment used includes: a 3-neck round-bottom flask, a dean and stark, a thermometer, a 220V heating mantle, a weighing apparatus, a tripod stand, a beaker, a conical flask, and a mechanical stirrer. The reagents were purchased from BDH chemicals and were of analytical grade with an assay of 96%.

2.2 Methods

2.2.1 Extraction of Sesame seed oil

Hot water flotation was employed for the extraction [10]. The sesame seeds were cleaned to remove any foreign objects, ground into a paste and heated to 80–90 °C for 15 minutes while stirring. Then, enough boiling water was added to keep the ground sesame seeds suspended, and the mixture was boiled for a further 15 minutes before cooling. The top oil layer was collected and gently heated to dry it.

2.2.2 Iodine value

In a clean, dry glass bottle with a glass stopper, 0.49 g of SISOMAR was dissolved in 15 ml of CCl_4 before 20 ml of Wijs solution was added. The bottle was sufficiently sealed by moistening the stopper with 10 % KI. Following the addition of 15ml of 10% KI solution and 10ml of distilled water, the bottle was left to stand for 30 minutes at a temperature range of 15 to 20 °C in a dark cupboard. 0.1 N $Na_2S_2O_3$ solution was then used to titrate the solution while using 1 % starch as an indicator. The discharge of a blue color made the eventual result clear. The iodine value was calculated using the formula:

$$I.V = \frac{12.69\ (v1-v2)}{w}\ x\ 0.1 \quad \text{… Equation (1)}$$

where, V_1 = Volume (ml) of thiosulphate solution used in the blank, V_2 = Volume (ml) of thiosulphate solution used in the test W = Weight (g) of sample [11].

2.2.3 Saponification value

In a volumetric flask, 2 g of the oil was weighed and dissolved in 25 ml of a 0.5 M alcoholic potassium hydroxide solution. The solution was now refluxed for 30 minutes with the flask attached to a condenser. The solution was allowed to cool, and the amount of acid needed was measured by titrating it against a 0.5 N HCl solution while it was still liquid. The blank titration was also conducted using the same approach. As a result, the saponification value was calculated:

$$Saponification\ value = \frac{28.05\ x\ (A-B)\ x\ F}{Weight\ of\ sample} \quad \text{… Equation (2)}$$

Where A= Blank titre value (cm^3), B= Sample titre value (cm^3) and F =Factor of 0.5 N HCl standard solution [12]

2.2.4 Density

This was calculated by using a weighing scale to calculate the weight of three equivalent volumes of SISOMAR within a density bottle. The following formula was used to compute the average densities:

$\rho = m / v$ … Equation (3)

where; ρ is density in g/cm^3, m = mass in g and v = volume in cm^3 [13]

2.2.5 Moisture absorption

Memmert desiccators were used to measure the moisture absorption of the SISOMAR resin film. In desiccators containing a saturated solution of 1g sodium chloride, 3g of the sample was added. The sample's wet weight was watched until it reached its maximum. The moisture absorption by resin was observed as the difference between the wet weight and dry weight [14]

2.2.6 Acid value

The SISOMAR sample was accurately weighed at 0.35 g on a watch glass, and then washed into a 450 ml beaker flask before being added 100 ml of ethanol. The solution was heated in a steam bath to boiling before two drops of phenolphthalein indicator were added. It was titrated against 0.1 N NaOH until a light pink color appeared, and then the solution was again heated in a steam bath to keep the pink color permanently. The reading from the burette was noted during the titration. The acid value was calculated thus:

$$Acid\ value = \frac{5.61\ x\ V}{W}$$ … Equation (4)

where, V = Volume (ml) of NaOH used and W = Weight of oil sample used [15].

2.2.7 Viscosity

The measurement was performed using a 100ml graduated glass micro syringe created by Phywe. The device was calibrated using a 20% (w/v) sucrose solution with a 2.0 mPa.S viscosity at 30 ℃. In comparison to the standard sucrose solution at 30 ℃, the resin's viscosity was assessed. For each sample, three readings were collected, and the average value was computed [7]

2.2.8 Synthesis of the alkyd resin from Sesame seed oil

The synthesis of short alkyd resin (40 % oil length) used calcium oxide as a catalyst. The following apparatus were used: a heating mantle, a 3-neck round-bottom flask, a mechanical stirrer, a nitrogen intake, and a thermometer inlet. Xylene was also utilized as the azeotropic solvent to remove any water that might have been generated during the trans-esterification procedure. The process was divided into two steps: polycondensation and alcoholysis-transesterification.

The first phase which is alcoholysis-transesterification, a 500 ml three-neck round-bottom flask was loaded with an accurately measured quantity of sesame oil (120 g), and then 0.3 g of calcium oxide and 71.09 g of glycerol were added. The temperature was then gradually raised to a temperature of 200 ℃ and kept constant for 2 hours. As the reaction advanced, portions were continuously taken at 30-minute intervals to verify for the formation of a clear solution which indicate the formation of monoglyceride. The resulting mixture was then allowed to cool to about 120 ℃ so that the trans-esterification stage could be initiated, 108.91 g of phthalic anhydride were added to the reaction mixture to begin the polycondensation phase, and 30 g of xylene were added to help form an azeotrope and assist in eliminating the water of esterification [5]. The temperature was raised to between 230 and 250 ℃ as the reaction continued. In order to calculate the drop-in acid value and the volume of water eliminated, aliquots from the reaction blend were obtained every 30 minutes. Titrating two aliquot parts of the mixture against 0.1M KOH gave the drop-in acid readings. solution, the indicator was phenolphthalein, which was measured out and dissolved in a 1:1 mixture of ethanol and toluene. When the acid value dropped to less than 10 mg KOH/g, the reaction was stopped [16].

2.2.9 Instrumentation

The thermal properties of the resin sample were investigated using thermo-gravimetric analysis (TGA) in an argon environment at a heating rate of 10 ℃/min from 300 to 900 ℃ using the PerkinElmer TGA model. Thermogravimetric analysis (TGA) is used to determine changes in mass with regard to temperature.

The STAR - SC/DTA F3 JUPITER instrument (NETZSTH, Germany) model was used to perform differential scanning calorimetry at temperatures between 200 ℃ and 250 ℃ in a nitrogen atmosphere. By examining how temperature affects a material's heat capacity, it is a technique for thermal analysis. Changes in the heat flow that occur from variations in the sample's heat capacity can be observed when a known mass sample is heated or cooled. This enables the observation of transitions such as the melt-to-glass transition (T_g), melting point (T_m), and the degree of crystallization (T_c) [4].

3. Results and Discussion

3.1 Results

The physiochemical properties of the *Sesamum* seed modified alkyd resin oil is shown in Table 1. The differential thermal analysis and differential scanning calorimetry of the 40 % alkyd resin has also been presented in Figures 1 and 2 respectively.

Table 1. Physico-chemical properties of *Sesamum indicum* seed oil Modified alkyd resin

Parameter	40 % alkyd resin
Iodine value (gI_2/100g)	70.2
Saponification value (mg KOH/100g)	227.5
Density (g/cm^3)	0.953
Moisture absorption (%)	0.22
Acid value mg KOH/g	9.23
Viscosity (m.Pa.s)	123.22

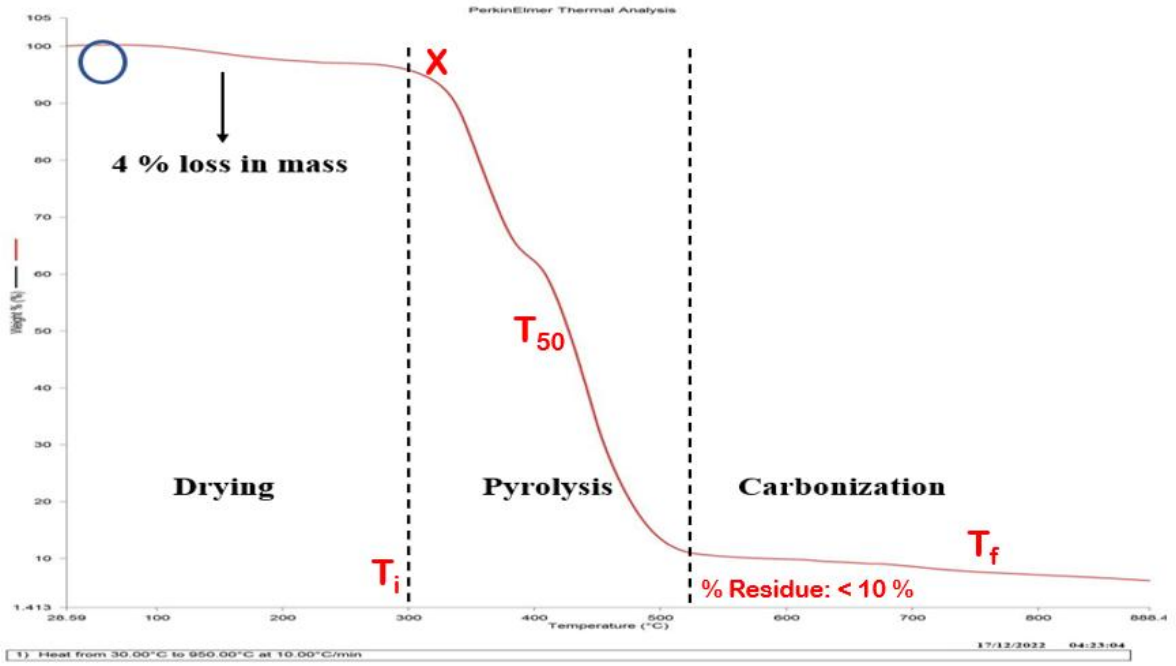

Figure 1. Differential thermal analysis of 40 % alkyd resin

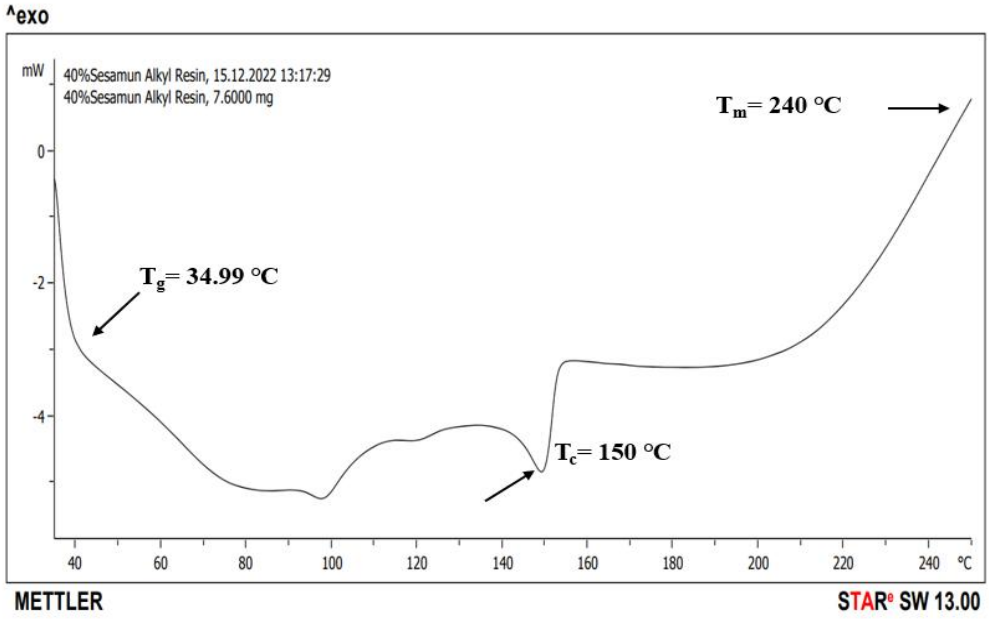

Figure 2. Differential scanning calorimetric analysis of 40 % alkyd resin

3.2 Discussion

3.2.1 Physicochemical properties of the 40 % alkyd resin

The synthesized alkyd resin had a density of 0.953 g/cm^3 which is less dense than water. The iodine value of 70.2 g I_2 /100g could be attributed to a reasonable degree of polymerization across the unsaturated alkyd chains. Sesame

seed oil (SISO) has been characterized to possess an iodine value is in the range of 120-150 g I_2 /100g [5]. It has also been reported by (Kalu) that sesame seed oil is of the semi-drying nature and as such, have various applications such as in the synthesis of alkyd resins for the paint industry and in the manufacturing of soap, whereas the non-drying oils are majorly employed as plasticizers [17]. The elevated saponification value of 227.5 mg KOH/100g was expected and could be attributed to the presence of ester linkages, it has been reported by [5] that SISO gave a saponification value of 172.13 mg KOH/100g. The moisture absorption capacity of the alkyd film 0.22 shows that the short oil alkyd will be less prone to permeability and thus improving performance and offering more resistance to blistering [7]. The higher acid value of 9.23 6.86 mg KOH/g of the SISOMAR was expected and could be attributed to a reasonable conversion of the fatty acids present in the SISO and addition of pthalic anhydride due to the carboxyl groups during the polycondensation phase, resulting to the alkyd polymer. It has been reported that SISO gave an acid value of 6.86 mg KOH/g and thus enhances its industrial application in the manufacture of paints and varnishes at less than 10 mg KOH/g acid values [5]. The viscosity of 123.22 conducted at 30 ℃ indicated that the synthesized alkyd resin could serve as a potential binder for the formulation of paints, similar results were obtained by [7]

3.2.2 Differential thermal analysis

Figure 1 shows that the 40% alkyd resin underwent thermal degradation in three stages: drying, pyrolysis, and carbonization (decomposition to char). About 4% of the mass was lost in the first step as shown (marked O), which could be ascribed to moisture evaporation and potential volatile organic compound emissions.

The second stage reveals that the thermal deterioration began at about 300 ℃ (marked x) and spread over a wide temperature range between 300 and 500 °C, which suggests that certain chemical species that may be identified using a TG-MS couple may have been removed. The initial degradation temperature (T_i) at 300 °C, final degradation temperature (T_f) at > 500 °C, temperature at which 50 % of the weight is lost (T_{50}) at ≤440, and the percentage of residue at 500 ℃ has also been shown. The temperature at the point of 50 % weight loss of the 40% alkyd resin which is a common indicator of the thermal stability of polymers was 440 ℃ indicating that the synthesized resin could meet the requirements for temperature resistance and be applied as surface coatings [18]

3.2.3 Differential scanning calorimetry

Figure 2 shows that the glass transition (T_g) value of the 40% alkyd resin is 34.99 °C, which is within the range of -93.5 to 226.85 °C typical of synthetic polymers. This value suggests the temperature at which the polymer changes from the glassy state to the rubbery state in the amorphous region [19]. Similar results have also been reported by (Ali Mutar et al., 2017). Polymer monomers absorb energy to arrange themselves into ordered configurations and crystallize at temperatures higher than T_g. It was observed as the lowest point of the dip since it is an exothermic process and takes less heat to keep the sample's temperature constant when compared to the reference. It can be seen that understanding these thermal properties is crucial for various industries, including material science, and product development.

Conclusion

The study revealed that alkyd properties such as iodine value, saponification value, density, moisture absorption, acid value and viscosity are essential to determining the suitability of an alkyd resin in serving as a binder for the coating industry and other industrial applications. SISOMAR exhibited likened properties of a conventional polymer as seen from differential thermal and scanning analysis curves, this could be attributed to an increase in thermal stability which could be tailored to performance and processing conditions of the polymer for potential industrial application.

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