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Production of Alkyd Resin from Selected Drying / Non-Drying Oil Blend: Correlative Study of Physicochemical Properties and Modelling

Chioma Ebelechukwu Nwobi-Okoye*, Victor Ifeanyi Ugonabo, Chigozie Francolin Uzoh
Department of Chemical Engineering, Nnamdi Azikiwe University Awka, Nigeria.
*Corresponding author's email: ebelenkem2000@gmail.com

Abstract
This study examines the production of alkyd resins from blends of drying oil (rubber seed oil, RSO) and chemically modified non-drying oil (palm kernel oil, PKO) to reduce after-yellowing associated with saturated lauric oils. Crude PKO, with an initial iodine value of 50.9 gI_2/100 g, was modified through epoxidation, hydroxylation, and hydration, achieving about 80% conversion of double bonds and reducing the iodine value to 15.8 gI_2/100 g. This modification improved colour stability and compatibility with RSO-rich alkyd systems. Oil blends (100% RSO, 100% modified PKO, 30:70, 50:50, and 70:30) were prepared, and their physicochemical properties were determined prior to polyesterification. Alkyd resins were synthesized via alcoholysis–polyesterification under controlled temperature and catalyst concentration, and the resulting resins were characterized for viscosity, acid value, iodine value, free fatty acid content, and colour. Higher RSO content increased iodine value and improved drying behaviour. Process modelling using Response Surface Methodology (RSM) was carried out for 30DPKO:70RSO and 50DPKO:50RSO blends to evaluate percent yield, drying index, and viscosity. Strong correlations between experimental and predicted results were obtained for the 30DPKO:70RSO blend, while moderate to strong correlations were observed for the 50DPKO:50RSO blend. Overall, the results confirm that desaturated PKO blended with RSO is suitable for alkyd resin production, yielding resins with improved drying performance, stability, and reduced after-yellowing.

Keywords: Alkyd resin; rubber seed oil (RSO); palm kernel oil (PKO); desaturated palm kernel oil (DPKO); Physciochemical properties; Correlation; RSM; D-optimal Design

1. Introduction

Alkyd resins are oil-modified polyesters produced through the polycondensation of polyhydric alcohols and polybasic acids or their anhydrides in the presence of fatty acids (Ikhuoria et al., 2004; Otabor et al., 2019). The incorporation of fatty acids imparts film-forming ability, flexibility, and air-drying characteristics, making alkyds one of the most widely used binders in surface coatings. Due to their low cost, ease of processing, solubility in common organic solvents, and good balance of mechanical and aesthetic properties, alkyd resins remain indispensable in decorative paints, varnishes, inks, and protective coatings (Manczyk and Szewczyk, 2002; Uzoh et al., 2018).

Considerable research has focused on the influence of drying oils such as linseed and soybean oils on alkyd resin performance, owing to their high unsaturation and ability to undergo oxidative crosslinking. These oils enhance curing rate, film hardness, and mechanical strength. Conversely, non-drying oils, rich in saturated fatty acids, are known to improve flexibility, gloss, and resistance to cracking but contribute little to oxidative curing. While several studies acknowledge that blending drying and non-drying oils can balance these properties, existing literature largely treats this approach qualitatively, with limited systematic investigation into how controlled blending affects both the physicochemical properties of the oils and the resulting alkyd resin performance. More importantly, most published works rely on conventional edible oils or fully drying oils, often overlooking underutilized, non-edible oil resources that could reduce cost, enhance sustainability, and limit competition with food supply. In Nigeria and many other developing economies, the dependence on imported

linseed oil for alkyd resin production remains economically burdensome, despite the availability of locally sourced alternatives. Rubber seed oil (RSO), a semi-drying oil obtained from *Hevea brasiliensis*, is abundant in southern Nigeria and possesses a level of unsaturation comparable to linseed oil (Aigbodion and Pillai, 2000). Yet, despite its availability and favorable chemical characteristics, RSO remains underexploited in industrial alkyd resin formulations.

Existing studies on RSO-based alkyds have primarily focused on its standalone use, with limited attention paid to strategic blending with non-drying oils to fine-tune resin properties. In addition, there is a notable lack of studies that combine oil blending strategies with quantitative modeling and optimization of the alkyd synthesis process. As a result, the relationships between oil composition, processing conditions, and final resin properties are not sufficiently understood, limiting the ability to design alkyd resins with targeted performance characteristics. This study addresses these gaps by synthesizing alkyd resins via the monoglyceride process using rubber seed oil (RSO), desaturated palm kernel oil (DPKO), and their blends. Unlike previous works, this research systematically evaluates how blending a semi-drying oil (RSO) with a modified non-drying oil (DPKO) influences key physicochemical properties of both the precursor oils and the resulting alkyd resins. Furthermore, the study incorporates process modeling and optimization, providing a quantitative framework for understanding and controlling alkyd resin properties. By doing so, this work not only demonstrates the technical viability of locally sourced, non-edible oil blends but also offers a pathway toward more sustainable, cost-effective alkyd resin production tailored to industrial coating applications.

2. Materials and Methods

2.1 Raw Materials and Experimental Controls

Rubber seed oil (RSO) and palm kernel oil were procured from the same certified local vendors in Benin City, Nigeria, to minimize variability arising from source differences. Palm kernel oil was desaturated prior to use to reduce its inherent non-drying characteristics and to enable systematic comparison with the drying oil (RSO). Analytical-grade glycerol, phthalic anhydride, lead oxide, sulphuric acid, xylene, sodium hydroxide, potassium hydroxide, and sodium chloride were used without further purification to ensure consistency with standard alkyd synthesis protocols. Distilled water was used throughout all experiments. Unblended oils (100% RSO and 100% desaturated palm kernel oil, DPKO) were used as control samples to benchmark the influence of oil blending on alkyd resin properties. All physicochemical analyses were conducted according to standardized American Oil Chemists' Society (AOCS, 1996) methods to ensure comparability and reproducibility with existing literature.

2.2 Preparation of Alkyd Resin Samples

Alkyd resins were synthesized via a controlled polyesterification process following established procedures reported by Otabor et al. (2019) and Aigbodion and Pillai (2001). These methods were selected because they are widely validated for oil-based alkyd resin synthesis and allow meaningful comparison with previous studies. Blends of RSO and DPKO were formulated at fixed ratios of 100:0, 70:30, 50:50, 30:70, and 0:100 (RSO:DPKO). These blend ratios were chosen to systematically investigate the transition from drying to non-drying oil behavior and to assess the progressive influence of unsaturation on resin properties. All synthesis reactions were carried out under identical conditions of temperature, reaction time, catalyst concentration, and stirring rate to ensure that observed variations in resin properties could be attributed primarily to oil composition rather than process fluctuations. Each alkyd formulation was synthesized in triplicate, and the average values were reported to improve reliability and reduce experimental error. Reaction yield and physical appearance were monitored throughout the polyesterification process to ensure consistency across batches.

2.3 Characterization of RSO/DPKO-Based Alkyd Resin Samples

The synthesized alkyd resins were characterized using standard physicochemical tests recommended by AOCS (1996). Parameters evaluated included colour, acid value, saponification value, iodine value, viscosity, and functional group composition using FTIR spectroscopy. All measurements were performed at least **three times**, and mean values were used for data analysis to enhance repeatability.

2.3.1 Determination of Free Fatty Acid (FFA)

The free fatty acid content of the oils was determined by titration using phenolphthalein as an indicator. This method was selected because FFA content directly influences alkyd resin synthesis efficiency and final resin stability. The relationship between acid value and FFA was applied as:

2FFA =Acid Value

$$\text{FFA} = \frac{Acid\ Value}{2}$$

Triplicate determinations were carried out for each oil sample, and consistent endpoint colour change was used as a control for accuracy.

2.3.2 Determination of Saponification Value

Saponification value was determined to assess the average molecular weight of the fatty acids in the alkyd resins. A fixed sample mass (2 g) and reagent volumes were used for all determinations to ensure comparability. Blank titrations were conducted alongside sample analyses to correct for reagent consumption and improve accuracy. The use of refluxing ensured complete reaction between the alkyd sample and alcoholic potassium hydroxide.

The saponification value was calculated using:

$$\text{Saponification Value (number)} = \frac{(V_2 - V_1) \times 56.1}{W}$$

Where;

56.1 = Molecular mass of potassium hydroxide
V_2 = Titre value of blank
V_1 = Titre value of sample
W = Weight of the sample used

All measurements were performed in triplicate, and deviations between repeats were maintained within acceptable analytical limits.

2.3.3 Determination of Iodine Value

The iodine value was determined following ASTM D4067-86 (1986) using the Wijs method, which is widely accepted for evaluating unsaturation in oils and resins. A fixed reaction time of 30 minutes and storage in the dark were employed to prevent iodine degradation and ensure reaction completeness. Blank determinations were conducted to serve as experimental controls.

Iodine value was calculated as:

$$\text{Iodine value} = \frac{(V_2 - V_1) \times 12.69}{Weight\ of\ sample\ (w)}$$

Where 12.69 = molecular mass of iodine
V_2 = Blank titre value
V_1 = sample titre value
W = Weight of the sample

Each determination was repeated three times, and the average value was reported to improve reliability.

2.3.4 Viscosity Measurement

The viscosity of the synthesized alkyd resins was measured using an Ostwald viscometer at a controlled spindle speed of 60 rpm. This speed was selected to ensure stable flow behavior while avoiding shear-induced structural changes in the resin. Measurements were conducted at ambient temperature, and the viscometer was cleaned and calibrated between samples to avoid cross-contamination. Triplicate measurements were taken for each sample, and mean values were reported.

2.3.5 FTIR Spectroscopy

FTIR spectroscopy was used to confirm the formation of ester linkages and other functional groups characteristic of alkyd resins. Spectral analysis was carried out using a Buck FTIR spectrometer (Model Cary 530) over a wavenumber range of 500–4000 cm^{-1}. This range was selected to capture key absorption bands associated with hydroxyl, carbonyl, and aliphatic groups. Duplicate scans were recorded for each sample to confirm spectral consistency.

2.4 Statistical Analysis

Experimental data obtained from the polyesterification runs were analyzed using Response Surface Methodology (RSM) to assess the individual and interactive effects of process variables on resin yield, drying index, and viscosity. A second-order polynomial regression model was fitted using the least-squares technique. The reliability of the model was evaluated through ANOVA, lack-of-fit tests, and goodness-of-fit indicators including R^2, adjusted R^2, predicted R^2, and adequate precision.

Statistical significance was assessed at a 95% confidence level ($p < 0.05$). Model adequacy and data reliability were further verified using residual and normal probability plots to confirm homoscedasticity, independence, and normal distribution of errors.

3. Results and Discussion

3.1 Physicochemical Properties of the Oils

Table 1 summarizes the physicochemical properties of rubber seed oil (RSO), palm kernel oil (PKO), and desaturated palm kernel oil (DPKO). The observed color differences—dark brown for RSO and golden yellow for PKO—are typical of non-refined drying and lauric oils, respectively, and are relevant because oil color directly influences the appearance of the resulting alkyd resins and their suitability for surface coating applications. The lighter color of DPKO after modification is particularly advantageous for producing alkyds with improved aesthetic quality, as similarly reported for chemically modified lauric oils used in coatings. The higher acid value of RSO compared to PKO reflects its greater degree of unsaturation, which increases susceptibility to oxidative degradation and hydrolytic cleavage of triglycerides. This trend is consistent with reports on other drying oils such as linseed and soybean oils, where higher unsaturation is typically associated with elevated free fatty acid content. In contrast, PKO, being rich in saturated lauric and myristic acids, exhibits lower acidity and greater inherent stability.

The significantly higher saponification value of PKO relative to RSO indicates the presence of shorter-chain fatty acids and lower molecular weight triglycerides. This characteristic is well known for lauric oils and has been widely reported to enhance reactivity during alkyd synthesis due to a higher density of ester-forming sites. The modification process applied to PKO further increased its saponification value while reducing its acid value, confirming successful chemical alteration and improved suitability for controlled polyesterification reactions. Iodine value measurements clearly differentiate the oils in terms of drying potential. RSO exhibited a high iodine value (144.8 gI_2/100 g), classifying it as a strong drying oil, whereas PKO showed a much lower value (50.9 gI_2/100 g), consistent with its non-drying nature. After desaturation, DPKO displayed a markedly reduced iodine value (15.8 gI_2/100 g), indicating a substantial reduction in unsaturation. This reduction enhances oxidative stability and allows DPKO to function as a moderating component in blended alkyd systems, similar to the role reported for hydrogenated or epoxidized vegetable oils in alkyd formulations. Overall, these results demonstrate that blending highly unsaturated RSO with chemically stabilized DPKO offers a strategic means of balancing drying ability, reactivity, and stability in alkyd resin production.

3.2 Physicochemical Properties of Alkyd Resin Samples

The physicochemical properties of the synthesized alkyd resins are presented in Table 3. A noticeable improvement in resin color was observed with increasing DPKO content, confirming that oil modification effectively translates into lighter-colored alkyds. This is particularly important for coating applications where color clarity and reduced yellowing are required. The acid values of all alkyd samples fell within a narrow range (2.10–3.27 mgKOH/g), indicating a high degree of polyesterification across all formulations. Such low acid values are comparable to those reported for commercially acceptable short- and medium-oil alkyd resins and suggest efficient esterification with minimal residual free acids. The gradual decrease in acid value with increasing DPKO content can be directly linked to the lower acidity of the modified oil, which reduces side reactions and promotes more uniform polymer growth.

Saponification values increased with increasing DPKO content and were highest for the 100% DPKO-based alkyd. This behavior reflects the predominance of shorter-chain fatty acids in DPKO, which produce a higher concentration of ester linkages per unit mass of resin. Similar trends have been reported in alkyds synthesized from coconut and palm kernel derivatives, where higher saponification values are associated with improved solubility and processing characteristics. Iodine value trends among the alkyd resins provide clear insight into their drying behavior. The 100% RSO alkyd exhibited the highest iodine value, corresponding to rapid oxidative curing and the formation of harder films. This aligns with established understanding of drying oil alkyds, where high unsaturation promotes faster cross-linking through oxygen uptake. In contrast, the 100% DPKO alkyd displayed much lower iodine values, resulting in slower drying and the formation of softer, more flexible films.

For the blended alkyds, drying behavior followed the RSO content in the formulation (70% RSO > 50% RSO > 30% RSO). This demonstrates that drying performance can be systematically tuned through blend composition without compromising resin quality. Such controllable drying characteristics are advantageous for tailoring alkyd resins to different coating applications, ranging from fast-drying industrial finishes to flexible architectural coatings.

3.3 FTIR Characterization

3.3.1 FTIR Analysis of PKO and RSO

The FTIR spectra of PKO and RSO exhibited characteristic absorption bands typical of triglyceride-based vegetable oils. Strong ester carbonyl (C=O) stretching bands around 1740 cm^{-1} and aliphatic C–H stretching vibrations in the 2920–2850 cm^{-1} region confirm the triglyceride structure of both oils. Notably, RSO showed more pronounced C=C stretching near 1650 cm^{-1}, reflecting its higher unsaturation level. This spectral difference corroborates the iodine value data and aligns with previous FTIR studies of drying versus non-drying oils.

3.3.2 FTIR Analysis of RSO–DPKO Alkyd Resins

The FTIR spectra of the blended alkyd resins confirmed successful polyesterification through the presence of strong ester carbonyl peaks in the 1730–1740 cm^{-1} range and persistent aliphatic C–H stretching bands. Variations in the intensity of the C=C stretching bands among the blends provide molecular-level evidence of the compositional effects observed in the physicochemical data. Higher RSO content resulted in more pronounced unsaturation bands, indicating greater cross-linking potential, while higher DPKO content produced more saturated and structurally uniform resins. These observations are consistent with reports on blended oil alkyd systems, where FTIR analysis reflects controlled tuning of resin structure via oil composition.

3.4 Model Correlation and Predictive Accuracy

The regression model developed to predict resin performance showed strong agreement with experimental data, particularly for the 30DPKO:70RSO blend, where correlation coefficients exceeded 0.87 for yield, drying index, and viscosity. These high correlations indicate that the model effectively captures the relationships between blend composition and key resin properties. For the 50DPKO:50RSO blend, slightly lower but still robust correlation values were obtained, suggesting increased system complexity as the contribution of the modified oil increases. Nevertheless, the model remained reliable, demonstrating its applicability across different blend ratios. Predicted-versus-actual plots showed close alignment along the 45° line, while residual analysis confirmed the absence of systematic error. Taken together, these findings demonstrate that the regression model provides a dependable framework for understanding and predicting the behavior of alkyd resins derived from RSO–DPKO blends. While optimization was not pursued in this study, the strong predictive performance highlights the potential of this approach for future formulation refinement and scale-up.

3.5 Summary

This study demonstrates that chemically modified palm kernel oil can be effectively blended with rubber seed oil to produce alkyd resins with balanced drying behavior, improved color, and controlled reactivity. Compared with alkyds derived solely from drying oils, the blended systems offer enhanced formulation flexibility and performance tuning, aligning with trends reported in sustainable and bio-based coating research. The results provide a strong foundation for future optimization and application-driven development of environmentally friendly alkyd resins.

Table 1: physciochemical properties of the oils (rubber seed oil and palm kernel oil)

Physicochemical properties	Crude PKO	Crude RSO
Acid value(mgKOH/g)	1.8135	2.367
Iodine value (gI_2/100g)	50.904	144.8
Saponification value(mgKOH/g)	244.752	194.403
Free fatty acid(% as oleic acid)	0.860	1.189
Peroxide value(meq O_2/kg)	1.60	2.80
Viscosity (cp, 40°c)	37	55
Refractive index (25°c)	1.460	1.473
Specific gravity	0.915	0.921
Colour	Golden yellow	Dark brown

Table 2: Physciochemical properties of desaturated palm kernel oil

Parameter	Value
Colour	Pale yellow
Acid Value (mg KOH /g)	1.42
Saponification Value (mg KOH /g)	248.6
Iodine Value (gl2 /100g)	15.8
Free Fatty Acid (%)	0.71
Viscosity (mPas.s)	43.5

Table 3: Physicochemical properties of blended RSO/DPKO alkyd resin

Blend(RSO:DPKO)	Colour	Acid Value(mgKOH/g)	Saponification Value (mgKOH/g)	Iodine Value(gl_2/100g)	Free fatty acid	Viscosity (mpas-1)
100:0 (100%RSO)	Dark brown	3.27	224.603	110.354	1.6	3800.20
0:100 (100%DPKO)	light yellow	2.10	240.452	79.405	0.7	1600.30
70 :30	Brown	2.90	232.416	104	1.2	3200.30
50 : 50	Brownish yellow	2.60	235.378	95	0.95	2600.40
30 :70	Yellowish brown	2.30	238.452	88	0.82	2000.30

Table 4: FTIR peaks of RSO/DPKO alkyd resin blends

Wave number (cm^{-1})	Bond Source	Functional Group/vibration
2920-2850	C – H stretching	Aliphatic
1740-1730	C = O stretching	Ester carbonyl
1650-1630	C = C stretching	unsaturation (olefinic)
1460-1440	C – H bending	- CH_2 scissoring
1375-1360	C – H bending	-CH_3 symmetric bending
1160-1120	C – O – C stretching	Ester linkages
720	-(CH_2)n rocking	Long- chain methylene

4.0. Conclusion

Alkyd resins were successfully synthesized through a controlled polyesterification (monoglyceride) process using selected blends of a drying oil, rubber seed oil (RSO), and a non-drying oil, desaturated palm kernel oil (DPKO). The influence of blend composition on key physicochemical properties was systematically examined. Increasing the proportion of RSO resulted in higher iodine values and faster drying behavior, reflecting the increased degree of unsaturation and enhanced oxidative crosslinking. In contrast, higher DPKO content produced resins with lower acid values and improved processing stability, indicating more controlled esterification during synthesis. The consistently low acid values across all formulations confirm effective esterification and successful alkyd resin formation.

The study further showed that while higher RSO content improves drying characteristics, it also increases susceptibility to after-yellowing during aging, attributable to oxidative degradation of highly unsaturated components. Conversely, formulations containing higher levels of DPKO exhibited reduced after-yellowing, highlighting the role of oil modification and blend composition in improving oxidative and colour stability. These findings emphasize the importance of balancing drying performance and long-term appearance in alkyd resin formulation. Overall, the results demonstrate that blending drying and non-drying oils is an effective strategy for tailoring fundamental alkyd resin properties such as drying behavior, viscosity, and colour stability. However, the present study is limited to physicochemical characterization of the resins and does not include full coating performance validation. While the observed properties suggest that RSO–DPKO-based alkyds have potential as

alternatives to conventional oil-based alkyd resins, definitive claims regarding industrial applicability require further investigation.

Specifically, future work should include standardized coating performance tests such as film hardness, adhesion, impact resistance, chemical and weathering durability, as well as comparative evaluation against commercial alkyd resins. In addition, cost analysis and life-cycle considerations will be necessary to properly assess economic and industrial feasibility. The regression models developed in this study ($R > 0.87$) provide a reliable predictive framework for understanding composition–property relationships and can support future optimization studies aimed at enhancing performance consistency, scalability, and practical coating applications.

Declaration of Generative AI and AI-assisted technologies in the writing process

During the preparation of this work the author(s) used ChatGPT in order to correct the grammar and rewrite some sentences. After using this tool/service, the author(s) reviewed and edited the content as needed and take(s) full responsibility for the content of the publication.

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