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The Novel Application of Organosolv Lignin Extracted from Eucalyptus Sawdust in the Synthesis of Alkyd Resin

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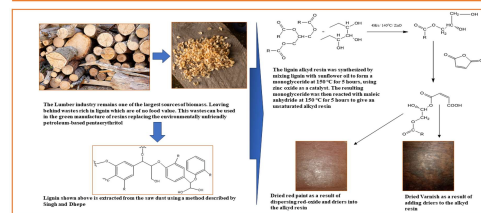
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Abstract: This study examines the potential of lignin as a feedstock for the green production of alkyd resins, taking advantage of an underutilized component of cellulosic biomass. The novel basis for this research is provided by the use of eucalyptus sawdust. The conventional production of polyester resins is based on petroleum-based pentaerythritol, which has a significant impact on the environment. Acidified methanol was used to synthesize flexible alkyd resins using organosolv lignin extracted from eucalyptus sawdust to address this issue. Maleic anhydride was used to react the resulting product, a monoglyceride, to produce an alkyd resin. A paint and varnish formulation was further incorporated with the resin. UV-Vis and FTIR spectroscopy was used in the study to quantitatively analyze resin, paint, film, and varnish, evaluating their optical properties and transmittance. The result was an alkyd resin that has optimal flexibility and excellent optical properties, making it suitable for use on diverse substrates. By reducing dependence on petroleum-based materials in paint and varnish formulations, this research contributes to a more sustainable manufacturing approach.

Keywords: Synthesis, Alkyd Resin, Monoglyceride, Lignin, Monoglyceride

THE NOVEL APPLICATION OF ORGANOSOLV LIGNIN EXTRACTED FROM EUCALYPTUS SAWDUST IN THE SYNTHESIS OF ALKYD RESIN



1. Introduction

The depletion of petroleum resources and related environmental issues are causing a rapid increase in the utilization of renewable feedstock for developing alternative materials. Lignin, the second major constituent of lignocellulosic biomass, is catching researchers' attention for synthesizing various value-added materials due to its renewable and biodegradable nature, large abundance, non-food value, and high functionality.¹

Lignocellulosic waste materials are the most promising feedstock for the next generation of a renewable, carbon-free substitute for existing liquid fuels. Concerns about the depletion of fossil fuel resources and climate change attributed to anthropogenic carbon dioxide emissions are driving a strong global interest in renewable carbon-free energy sources from these sources.²

In many hydroxyl groups, lignins are intensively studied as candidates to substitute fossil-based alcohol and polyol components in polyurethanes, alkyds, epoxides, and phenol-formaldehyde resins.^{3,4}

Agricultural feedstocks such as oil palm, sugarcane bagasse, and corn are receiving much interest since such sources can be used for the industrial production of fuels. However, these compete for arable land with crops intended for human or animal consumption, putting pressure on food prices and accelerating environmental degradation.⁵ Thus, current

research interest is focusing on cellulosic biomass from sources that do not compete with food crops such as water hyacinth, banana pseudostems, rice straws, sugar cane bagasse, wheat straw, rice stalk, cotton linters, forest thinning, or novel crops that can be grown in environments too marginal for food production, such as switchgrass and eucalyptus.⁶

Development of technologies that enable the economical production of suitable compounds from these sources is necessary for biomass to be sustainable for fuel. Because of its surface-active properties, lignin has found low-value commercial applications.⁷ However, lignin has the potential to be an important feedstock for high-value products if it can be effectively separated from cellulose and hemicellulose.⁸ Advances in biorefinery technologies and lignin valorization have opened new opportunities for lignin utilization as a source of renewable chemicals and fuels.⁹

Lignin is primarily employed in polyurethane foams, followed by elastomers and adhesives, rarely in other polyurethane fields. However, by adapting the composition and the ratio of the hard and the soft blocks, alkyd resin can be customized to its application.¹⁰ They find use as coatings, adhesives, sealants, and elastomers (CASE) and in several medical applications such as catheter and general-purpose tubing, hospital bedding, surgical drapes, wound dressings, and a variety of injection-molded devices as they are cost-effective and provide for more longevity and toughness.¹¹ Because of

its renewability, abundance, and low cost, lignin is a good functional additive in polymers such as alkyds.

Developing environmentally friendly, easy-doped, and low-cost, functional filler for alkyd resin based on lignin is a meaningful and high value-added utilization for lignin.¹² In this study, organosolv lignin was isolated from eucalyptus sawdust using acidified methanol as the extracting solvent and used to prepare unsaturated alkyd resin films. Optical properties, thermal properties, and functional groups were analyzed using an Ultraviolet-visible light spectrophotometer (UV-Vis) and a Fourier-Transform Infrared spectrophotometer (FT-IR).

Lignin's abundance and renewability make it a promising candidate for various industrial applications. The most common source of lignin is Kraft lignin, which is obtained from black liquor during the Kraft pulping process.¹³ Structurally, lignin is a complex polymer of three phenylpropane monomers linked through different types of chemical bonds.¹⁴ As a three-dimensional amorphous and branched polymer, lignin is known for its hydrophobic nature, making it an ideal material for water-resistant coatings and adhesives.¹⁵ The methoxy and hydroxyl functional groups in lignin make it a promising precursor for producing various chemicals, including vanillin, phenol, and renewable fuels.¹⁶ Lignin is the second major constituent of lignocellulosic biomass and has caught the attention of researchers due to its renewable and biodegradable nature, large abundance, non-food value, and high functionality.^{2,3} Industrially, lignin is available as so-called Kraft lignin from black liquor, a by-product of the Kraft pulping technology.¹⁷ Structurally, lignin is a randomly cross-linked polymer with three phenyl propane derivatives mainly linked by ether bonds.¹⁸

Lignin has physical and biological functions in the tree, such as forming the cell wall hydrophobic part, protection against microbiological degradation, and cementation between cell layers. It also induces stiffness in the wood cell walls.⁷ This hydrophobic biopolymer is placed between the cellulose and has a phenolic plastic function in the wood. Lignin contains both phenolic and non-phenolic aromatic structures with conjugated aliphatic double bonds. Lignin from softwood is based almost exclusively on coniferyl alcohol, which has one methoxy group per aromatic ring; nonetheless, hardwood lignin is made of a mixture of coniferyl alcohol and sinapyl alcohol, which has two methoxy groups per aromatic ring.^{7,18} Lignin's characteristics of being agricultural-based, abundantly available, low-cost, renewable, nontoxic, moderately biodegradable, eco-friendly, and containing high functionality of -OH groups make it an important material of choice in synthesizing alkyd resins. Alkyd resins, which are low molecular weight esters formed when polyhydric alcohols react with polybasic and monobasic acids, are widely used in air-drying decorative gloss paints, and can be modified to give a range of properties.

The -OH groups in lignin provide good reacting sites toward the oil and maleic anhydride. Moreover, lignin has been

shown to confer good ultraviolet and heat resistance to alkyd resins, leading to superior gloss and color retention compared to other resins of similar oil strength.¹⁹ The higher content of chemically stable carbon-carbon bonds in softwood lignin causes different properties, such as slower delignification in chemical pulping compared to other types of lignin.²⁰

Due to its aromatic network, lignin is the most UV-absorbing component of wood, making it the most affected when exposed to exterior conditions. The rapid oxidation of lignin compared to carbohydrates makes it more susceptible to decomposition.^{21,22,23}

The degradation of outdoor wood surfaces is primarily due to the decrease in lignin concentration caused by oxidation^{22,24} (Figure 1). In addition to oxidation, hydrolysis is another important chemical reaction that attacks hydrolytically unstable acetal linkages in carbohydrates and aryl ether linkages in lignin. This reaction causes significant chemical changes in wood structures. It decreases wood density and causes the fiber to separate from wood structures, producing Kraft lignin^{19,25} (Figure 2).

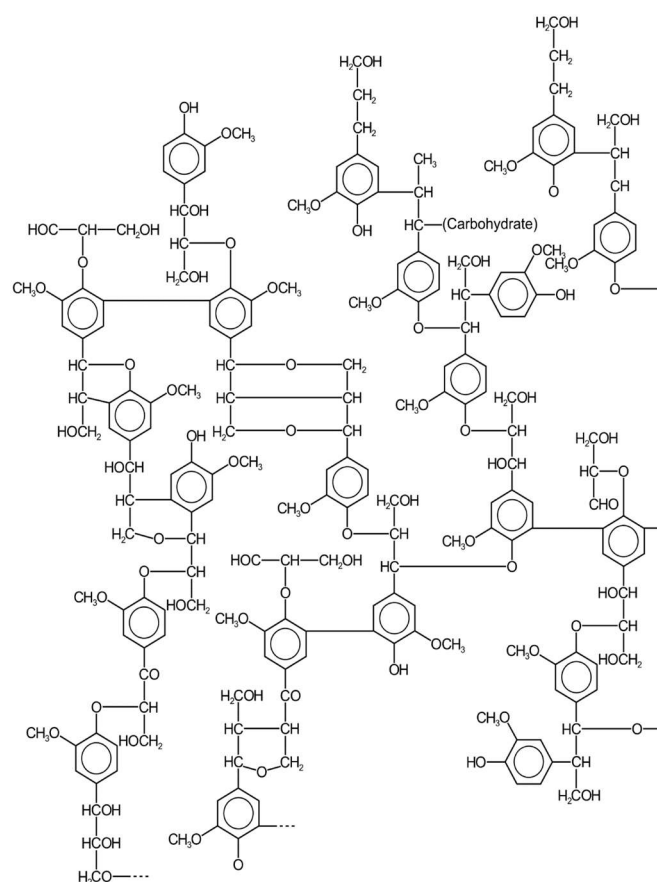


Figure 1. Lignin structures as hypothesized by Lawoko *et al.* 2006 [19].

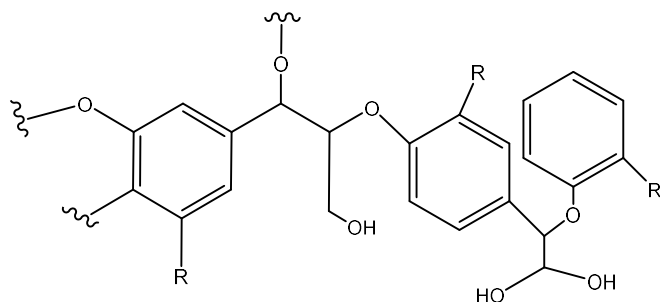


Figure 2. Kraft Lignin.

Objective

The objective of current study is to synthesis and qualitatively analysis alkyd resin from extracted organosolv lignin as a sustainable alternative to pentaerythritol in resin synthesis. Recent studies have shown that using pentaerythritol in alkyd resin synthesis is expensive and can result in gelation, limiting its use in short oil alkyds.^{26,27} In addition, environmental regulations regarding volatile organic compound emissions have led to a predicted decline in the demand for alkyd resin with pentaerythritol by 0.5% annually.²⁸ From the other side of view, pentaerythritol is known to be a significant non-point source of soil pollution due to its high mobility in soil.^{29,30} Thus, there is an urgent need for a sustainable alternative to pentaerythritol in alkyd resin synthesis.

The amorphous nature of lignin in the synthesized resin provides high flexibility, making it capable of accommodating varying temperature conditions on different substrates, such as iron sheets. Moreover, the resin penetrates the pores of substrates like concrete. It expands, resulting in better adhesion, making lignin resin an environmentally friendly and cost-effective alternative to conventional resins, as lignin is a cheap, renewable, abundant, and biodegradable resource.

2. Experimental

Sampling and sample preparation

Sawdust was obtained from a local wood mill after cutting eucalyptus lumber. The sawdust was ground into a fine powder using a plant mill and stored in a sealed bag. The samples were collected in Juja, Kenya, and the research project was conducted in the Jomo Kenyatta University of Agriculture and Technology (JKUAT) chemistry laboratory. The finely ground sawdust was sieved using a normal sieve and a tea sieve, and any unwanted materials were removed from the material that passed through the sieve.

Extraction

Lignin was extracted from the eucalyptus sawdust using a method described by Singh and Dhepe,¹⁶ with some modifications from Garcia et al.,³¹ Two hundred grams of ground samples were placed in a two-litre flask, and 300 ml of methanol, 23 g of analytical sodium hydroxide pellets, and 300 ml of water were added. The mixture was heated at 90 °C for 10 h, and the lignin present in the extracting solvent was

concentrated using a rotary evaporator to remove the extracting solvent. A separating funnel was used with hexane-ethyl acetate (1:1 v/v) as the organic solvent to separate the hydrolyzed lignin. The non-hydrolyzed lignin in the organic phase was concentrated and used to synthesize lignin alkyd resin.

Synthesis and formulation

The lignin alkyd resin was synthesized by mixing lignin with sunflower oil to form a monoglyceride at 150 °C for 5 h, using zinc oxide as a catalyst. The resulting monoglyceride was then reacted with maleic anhydride at 150 °C for 5 h to give an unsaturated alkyd resin.^{16,32}

The titanium dioxide pigment was dispersed in the resulting alkyd resin, driers were added to it, and thoroughly blended at high speeds of up to 1400 rpm to create paint. The remaining portion of the alkyd resin was mixed with driers to create varnish. The paint and varnish were applied to both wood and metal surfaces, and the qualitative properties of the film were analyzed after being scraped off.

Qualitative analysis

The optical properties of the resin, films, varnish, and paint were evaluated using a Shimadzu UV-VS 1800 spectrophotometer in the 200-800 nm range to determine their UV-Vis absorption spectra.³³ The Fourier Transform Infrared (FT-IR) spectra of the resin, films, paint, and varnish were analyzed using a Shimadzu FT-IR spectrophotometer, Model FTS-8000. KBr pellets of the samples were prepared by grinding 10 mg of the sample with 250 mg of KBr (FT-IR grade) and compressing them at 75 kN.cm⁻² for 3 min to produce 13 mm KBr pellets. The spectral resolution was set at 4 cm⁻¹, and the scanning range was from 400 to 4000 cm⁻¹.^{34,35}

3. Results and Discussion

UV visible characterization of kraft lignin and synthesised resin

The spectra from the resin and Kraft lignin were obtained and compared side by side to check the changes in conjugation, showing how the reaction took place. Figure 3 represents the absorption spectra of the resin and Kraft lignin.

This was done using a Shimadzu UV-VS 1800 spectrophotometer in the range of 200-800 nm [33] in a spectral scan.

Analysis of the UV Spectra

The spectrum attributed to kraft lignin shows a prominent shoulder peak at 250-300 nm. This peak can be associated with the presence of conjugated aromatic chromophores, which are a characteristic feature of lignin. This is supported by Li et al. (2020) study.³⁶ They have investigated the UV-Vis absorption spectra of kraft lignin derived from different feedstocks, including hardwood and softwood. The researchers observed a prominent shoulder peak at

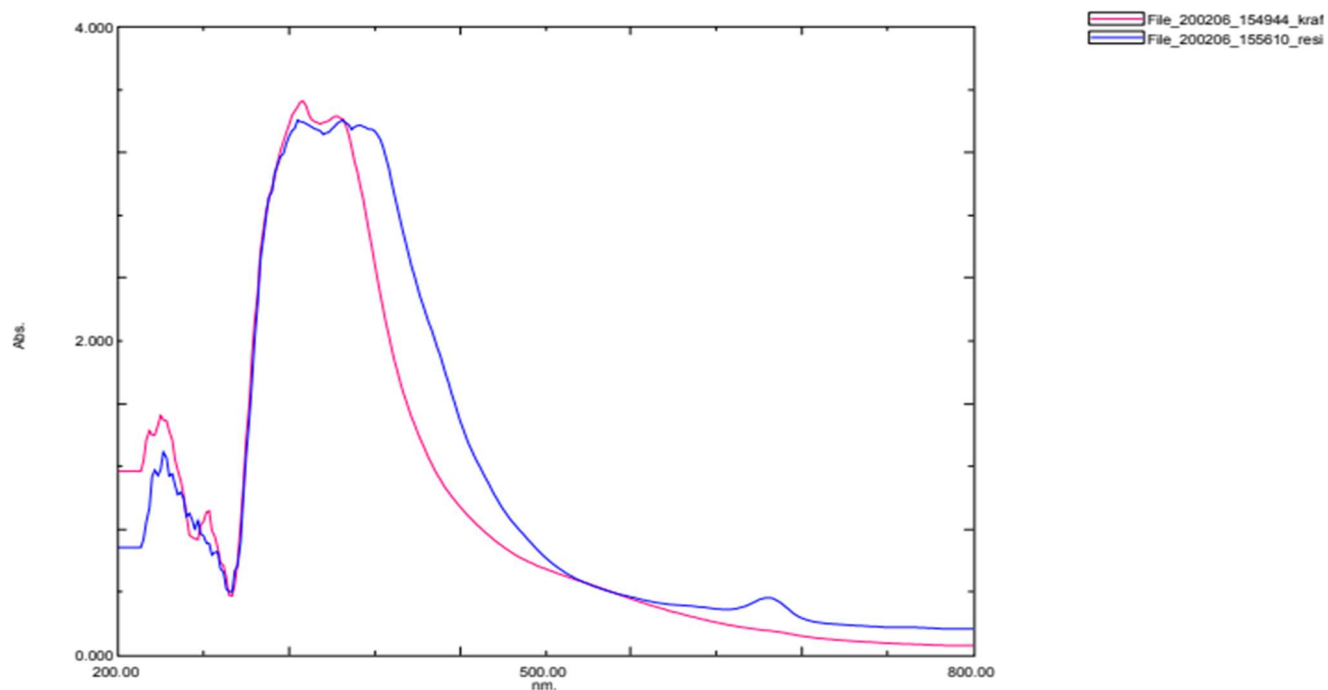


Figure 3. UV Spectra showing transmittance and various wave number ranges for Resin (blue) and Kraft lignin (red).

approximately 290 nm for hardwood and softwood kraft lignin samples. Another study by Zhang et al. focused on the UV-Vis absorption properties of lignin extracted from wheat straw.³⁷ In their research, a distinct peak was observed at around 300 nm in the UV region of the spectrum. This peak further supports the presence of aromatic chromophores in the lignin structure, contributing to its UV-Vis absorbance characteristics.

The appearance of these peaks in the UV-Vis spectrum of kraft lignin is due to the extensive conjugation of double bonds within the aromatic rings in the lignin structure. Light absorption in this wavelength range is associated with the π - π^* electronic transitions of the conjugated systems, resulting in the observed peaks.

The spectrum of the alkyd resin shows a broad absorption band from 250 nm to 450 nm. This results from conjugated double bonds and aromatic moieties derived from the lignin component. The presence of aromatic rings can be credited to absorption peaks in the UV-Vis spectrum. These peaks arise from the π - π^* transitions of the conjugated systems within the aromatic moieties.

These observations are supported by a study by Wang et al. investigated the UV-Vis absorption properties of alkyd resin synthesized from organosolv lignin.³⁸ The researchers observed a peak at around 220 nm, attributed to aromatic structures in the resin derived from the lignin precursor.

In a study by Zhou et al., the UV-Vis spectrum of alkyd resin synthesized from wheat straw lignin exhibited absorption peaks at approximately 230 nm and 270 nm, corresponding to aromatic chromophores.³⁹

These findings indicate that the synthesized alkyd resin retains some UV-Vis absorption characteristics associated with the aromatic structures in the original organosolv lignin precursor. These peaks' specific positions and intensities may vary depending on factors such as the lignin source, extraction method, and resin synthesis conditions.

In comparing the two spectra, the spectrum attributed to the resin shifts towards the higher wavelength due to increased conjugation. Thus, exhibiting a Bathochromic shift/redshift. This is because the ester resin is produced by reacting with maleic anhydride, which produces double bonds; see Figure 4.



Figure 4. A representation of the increase in conjugation from kraft lignin to alkyd resin.

There can also be observed a new peak at ~ 700 nm; this is usually attributed to a carbonyl group. The wavelength of ~ 700 nm in the UV-Vis spectrum typically corresponds to light absorption by chromophores containing a conjugated system with extended π -electron delocalization.

According to a recent study by Wu et al., an increase in the conjugation of lignin-based resins can be attributed to forming of ester bonds and incorporating functional groups, such as carboxyl and hydroxyl groups.⁴⁰ These functional groups can

contribute to the cross-linking of the resin and enhance its mechanical properties.

Similarly, Hu et al. study demonstrated that the conjugation of alkyd resins can be increased by incorporating unsaturated fatty acids.⁴¹ The double bonds in the fatty acid chains can participate in the cross-linking reaction, resulting in a more densely cross-linked resin with improved mechanical and adhesive properties.

These findings are consistent with the results obtained in this study, which showed increased alkyd resin conjugation due to

double bonds. The improved mechanical properties of the synthesized resin could be attributed to the increased cross-linking resulting from the double bonds formed during the reaction with maleic anhydride.

FTIR Characterisation of the Kraft Lignin and Resin

Figures 5 and 6 present the absorption spectra of the samples of the Kraft lignin and the resin, where the spectral resolution was set at 4 cm^{-1} and the scanning range from 400 to 4000 cm^{-1} .^{34,35}

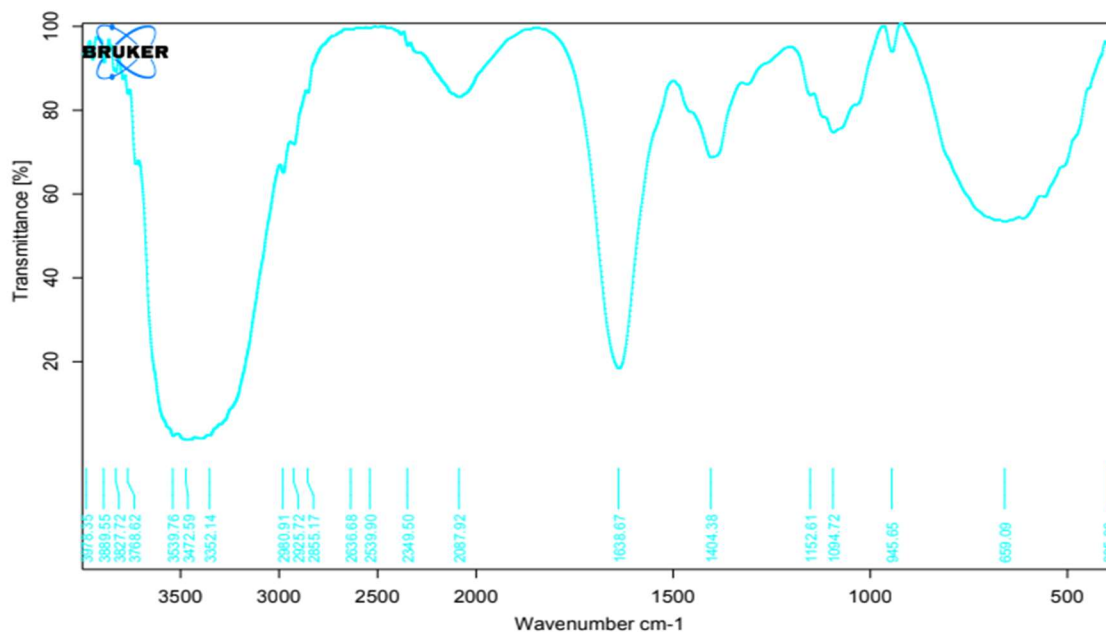


Figure 5. IR Spectrum showing transmittance and various wave number ranges for Kraft lignin.

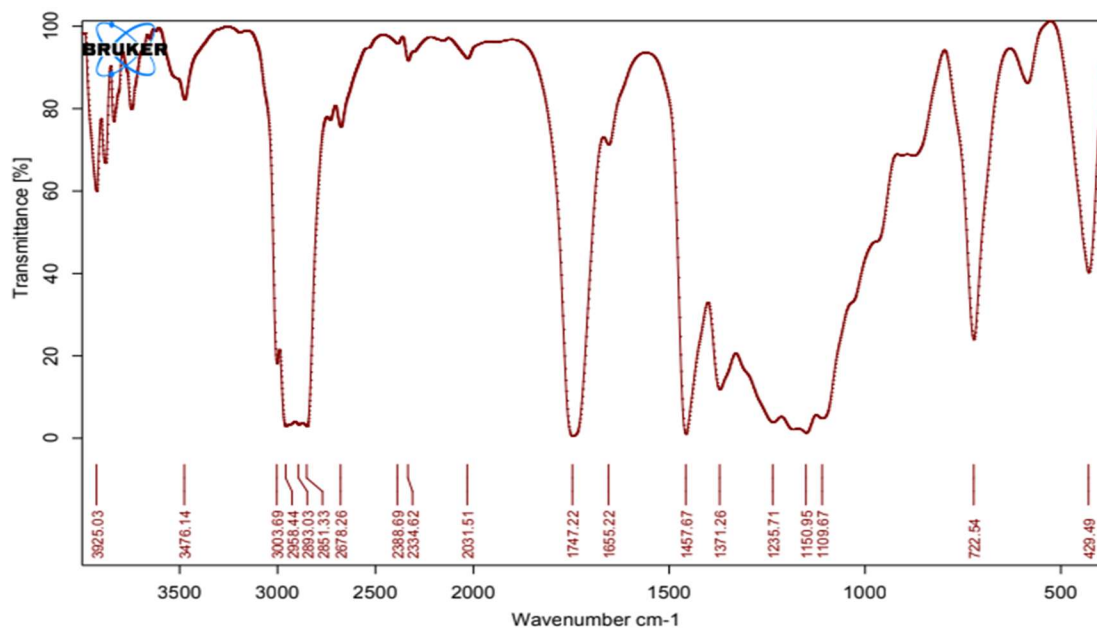


Figure 6. IR Spectrum showing transmittance and various wave number ranges for resin.

Analysis of kraft lignin FTIR spectrum

The extracted lignin contains some important chemical functional groups: methoxy, hydroxyl, carboxyl, and carbonyl.

Analysis of resin FTIR spectrum

There are a few new peaks to be observed, especially with the introduction of aromatic stretching and the introduction of an ester group.

Comparison of the spectra: Resin and kraft lignin

There is an increase in conjugation from the lignin to resin, and a new peak emerges stretching from 1645-1457 cm^{-1} , attributed to the formation of an ester group. This proves that the reaction among the lignin, maleic anhydride, and sunflower oil took place to give an alkyd resin.

Fourier Transform Infrared (FTIR) spectroscopy has been widely used to characterize lignin and its derived products. Ponce et al. reported that the FTIR spectra of kraft lignin showed characteristic peaks in 1740, 1609, 1515, and 1424 cm^{-1} , which corresponded to carbonyl, aromatic skeletal vibration, aromatic ring deformation, and C-H bending vibrations, respectively.³⁴ These peaks are consistent with the results observed in Figure 5, which showed that the Kraft lignin contained methoxy, hydroxyl, carboxyl, and carbonyl groups.

On the other hand, the FTIR spectra of the synthesized resin in Figure 6 showed a new peak stretching from 1645-1457 cm^{-1} , attributed to an ester group formation. This peak indicates the successful reaction between the lignin, maleic anhydride, and sunflower oil to produce an alkyd resin. Madivoli et al. reported that the formation of an ester group in alkyd resins could be identified by the appearance of a new band at around 1740-1720 cm^{-1} , which is consistent with the results observed in this study.³⁵

Moreover, the increase in conjugation from lignin to resin was also observed in the FTIR spectra. According to Madivoli et al., the increase in conjugation leads to a shift towards higher wavenumbers, consistent with the results observed in Figure 6.³⁵ This shift is attributed to introducing the aromatic stretching and the ester group. These results indicate that the alkyd resin was successfully synthesized from kraft lignin, which can be used as a sustainable alternative to petroleum-based alkyd resins in various applications.³⁴

One recent study that discussed the FTIR characterization of lignin and its derivatives was presented by Rana et al.,⁴² They investigated the effect of microwave-assisted pretreatment on lignin extracted from sugarcane bagasse and characterized the lignin using FTIR spectroscopy. The study found that the pretreatment led to the formation of new functional groups in the lignin, confirmed by the appearance of new peaks in the FTIR spectra.

Another recent study by Chen et al. investigated using lignin as a feedstock for synthesizing resins and coatings.⁴³ They used a lignin-derived polyol to prepare polyurethane coatings

and characterized them using FTIR spectroscopy. The study found that the coatings exhibited excellent adhesion and mechanical properties, indicating the potential of lignin as a sustainable alternative to petroleum-based materials in coatings and other applications.

Proposed chemical reactions for the synthesis of an alkyd resin from lignin and the formation of films from the alkyd resin using cobalt naphthalate are given in Figures 7 and 8.

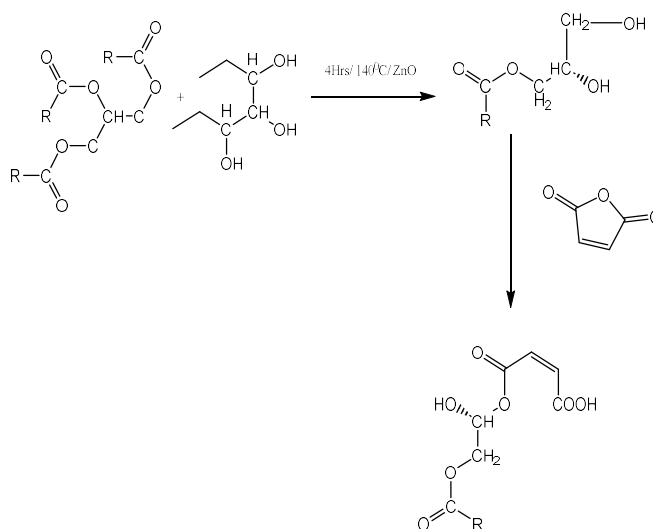


Figure 7. Proposed chemical reactions for the synthesis of an alkyd resin from lignin.

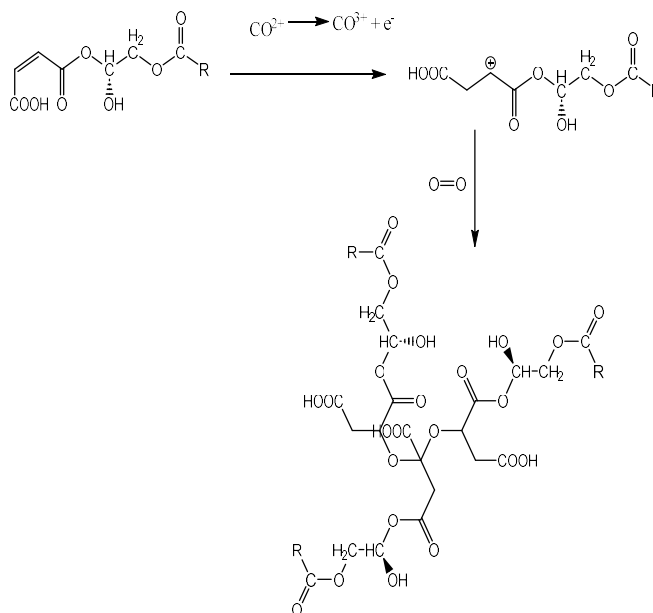


Figure 8. Proposed chemical reactions for the formation of films from the alkyd resin using cobalt naphthalate.

4. Conclusions

Eucalyptus sawdust, a by-product of the timber industry, has various uses in different sectors. It is commonly utilized as a

biomass fuel for generation of heat and energy. Eucalyptus sawdust is used as animal bedding in the poultry and livestock industries because of its absorbent properties. In composting, it is also utilized to enhance the decomposition process and produce high-quality compost. Particle boards and fiber boards used in construction and furniture manufacturing are produced using eucalyptus sawdust in the manufacturing sector.

Furthermore, it is utilized as mulch for weed suppression and soil moisture conservation in gardening and landscaping applications. Eucalyptus sawdust is used as a substrate for mushroom cultivation, which aids in the growth of different mushroom species. The versatile and potential of eucalyptus sawdust as a valuable resource is highlighted by these diverse applications.

Eucalyptus sawdust, as a lignin source for alkyd resin synthesis, has distinct advantages over other lignin sources. While lignin can be obtained from various biomass feedstocks, such as agricultural residues, hardwoods, and softwoods, eucalyptus sawdust has several advantageous features. Eucalyptus is a fast-growing and renewable resource that ensures a sustainable and readily available supply of sawdust.

Eucalyptus sawdust has a significant amount of lignin, which can be extracted efficiently using organosolv methods. The potential for alkyd resin production is enhanced by the high lignin content. Furthermore, eucalyptus lignin has unique chemical properties that could lead to alkyd resins with specific qualities like enhanced flexibility, improved adhesion, and optimal optical properties. By utilizing eucalyptus sawdust as a feedstock for alkyd resin synthesis, this study taps into the untapped potential of this underutilized lignin source, contributing to sustainable manufacturing practices while offering distinctive advantages over other lignin sources.

Increased conjugation from Kraft Lignin to the resin was observed in the FTIR spectra results. The UV-Vis spectra of the lignin and resin showed an increase in conjugation compared to the lignin.

The amorphous nature of lignin, which has many branched hydroxyl groups, makes it more flexible and facilitates better adhesion to the substrate applied. To achieve three-dimensional functionality, a tri-functional alcohol and di-functional acid are reacted to create a three-dimensional polymer.

Due to their high base strength and low volatility, the alkyd resin films formed were glossy and dried quickly, drying in approximately three hours. Alkyd stability and cross-linking reactions are improved by increasing the excess hydroxyl, making them ideal for enamel formulation and polyesters. Although newer resins have emerged in the last 25 years, alkyd resins remain the most produced solvent-soluble resin in the surface industry, primarily because of their versatility, low cost, and stability.

They can be modified to achieve various properties, from fast, hard-drying, low-flexibility products to slow-drying, soft, flexible films. Ester hydrolysis, susceptible to water, acid, and alkali, is typical of alkyd resins since they are polyesters. However, the ester structure provides excellent UV and heat resistance, resulting in superior gloss and color retention compared to similar oil-length epoxy (polyether) esters.

Based on the results of the study, it is recommended that further research should be conducted to explore methods for reducing the drying and curing time of alkyd resins derived from lignin without negatively impacting their color retention properties. This is especially important given that the high hydroxyl value of lignin can significantly slow down alkyd resin drying and curing process. Developing more efficient curing methods could lead to an increase in the practical applications of lignin-based alkyd resins in various industries, such as enamel formulation and polyester production. Additionally, future studies should investigate the potential of modifying the lignin molecule to decrease the number of hydroxyl groups and improve its compatibility with alkyd resins, thereby enhancing their overall performance.


Declaration of Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author Contributions

I, Peredy Khwesa, am the sole author of this work. All aspects of this document, including its conception, research, writing, and revision, are the result of my individual efforts and contributions.

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