UTILIZATION OF CRUDE GLYCEROL FROM BIODIESEL PRODUCTION FOR ULTRA-VIOLET CURABLE ALKYD RESIN PREPARATION VIA SOLVENT-FREE ENZYMATIC PROCESS

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UNIVERSITI SAINS MALAYSIA

2025

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by

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Thesis submitted to in fulfilment of requirement
for the degree of
Doctor of Philosophy

March 2025

ACKNOWLEDGEMENT

Firstly, I would like to express my special thanks to my supervisor, Professor Tay Guan Seng. He not only provided me with invaluable guidance and suggestions in academic research, but also selflessly cared for and supported me throughout the entire doctoral study process. Professor Tay's rigorous academic attitude and keen academic insight have greatly benefited me. He has given me comprehensive guidance in the selection of research directions, experimental design, data analysis, paper writing, and the publication of results, enabling me to continuously advance in the field of polymer research. Secondly, I would like to thank my associate supervisor, Professor Lee Chee Keong. Professor Lee's extensive knowledge and experience have provided me with a solid theoretical foundation for my research. He has greatly helped and guided me in research methods, experimental techniques, and statistical analysis. His meticulous opinions and constructive feedback have significantly improved the quality of my thesis. Thirdly, I would like to thank the lab instructors and office staff at School of Industrial Technology. They have given me a lot of help and support during my PhD program. I would like to extend my deepest respect to them. Finally, I would like to thank my family and friends for their understanding and support during my pursuit of a doctoral degree. Their encouragement and care have been the driving force behind my perseverance and determination to move forward courageously.

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LIST OF ABBREVIATIONS

ANOVA	analysis of variance
ATR	attenuated total reflectance
AV	acid value
CA	contact angle
CALB	*Candida antarctica* lipase B
CCD	central composite design
CL	ε-caprolactone
CRD	completely randomized design
DMSO	dimethyl sulfoxide
DXO	1,5-dioxepan-2-one
eROP	enzymatic ring-opening polymerization
FT-IR	Fourier transform infrared
GC	gas chromatography
GMA	glycidyl methacrylate
GPC	gel permeation chromatography
HDDA	1,6-hexanediol diacrylate
IAn	itaconic anhydride
KOH	potassium hydroxide
MG	monoglycerides
M_n	number average molecular weight
MONG	matter organic non-glycerol
M_w	weight average molecular weight
PAn	phthalic anhydride
PBS	polybutylene succinate
PBSI	poly (butylene succinate-co-itaconate)

PBT	polybutylene terephthalate
PDB	protein data bank
PGA	polyglycerol adipate
PGOS	poly (glycerol-1,8octanediol-sebacate)
PGS	poly (glycerol sebacate)
PHA	polyhydroxyalkanoate
PLA	polylactic acid
RSM	response surface methodology
SAn	succinic anhydride
SEM	scanning electron microscopy
TLL	*Thermomyces lanuginosus* lipase
TMPTA	trimethylolpropane triacrylate
TPGDA	tripropylene glycol diacrylate
UV	ultra-violet
wt%	weight percentage

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PENGGUNAAN GLISEROL MENTAH DARIPADA PENGELUARAN BIODIESEL UNTUK PENYEDIAAN RESIN ALKID YANG DIMATANGKAN DENGAN SINARAN ULTRAUNGU MELALUI PROSES ENZIMATIK TANPA PELARUT

ABSTRAK

Pengembangan pelapis ramah lingkungan telah menjadi kebutuhan mendesak untuk mengatasi masalah lingkungan dan pembatasan peraturan pada senyawa organik yang mudah menguap. Penelitian ini mengeksplorasi pendekatan enzimatik bebas pelarut baru untuk mensintesis resin alkid yang dapat disembuhkan dengan sinar Ultra-Violet (UV) menggunakan gliserol mentah yang berasal dari biodiesel, minyak kedelai, glisidat metakrilat, anhidrida itakonik, anhidrida ftalat, dan anhidrida suksinat. Proses sintesis dioptimalkan untuk memaksimalkan hasil monogliserida dan meningkatkan kinerja resin. Pertama, kelayakan penggunaan gliserol mentah dikonfirmasi melalui metanol dan analisis kandungan logam. Monogliserida kemudian disintesis melalui gliserolisis enzimatik bebas pelarut, dengan hasil monogliserida sebesar 28,93% setelah kondisi reaksi dioptimalkan dengan menggunakan metodologi permukaan respons (RSM). Selanjutnya, sistem bebas pelarut digunakan untuk pra-reaksi, reaksi enzimatik, dan pengawetan UV, yang mengarah pada sintesis film resin alkid yang dapat disembuhkan dengan UV, menghasilkan berat molekul rata-rata (M_n) dari resin sebesar 1144 g/mol dan kandungan gel film sebesar 91,1% dalam kondisi yang diinginkan. Sifat-sifat film yang diawetkan dengan UV kemudian dievaluasi. Meningkatkan rasio molar anhidrida suksinat terhadap anhidrida ftalat meningkatkan fleksibilitas, daya rekat, dan ketahanan benturan pada film, tetapi mengurangi kekerasan dan sudut kontak, sementara ketahanan pelarut tetap stabil. Studi ini menunjukkan bahwa integrasi bioresources, proses enzimatik bebas pelarut, dan pengawetan UV memungkinkan produksi resin alkid yang berkelanjutan, berkinerja tinggi, dan ramah lingkungan, sehingga mengurangi ketergantungan pada bahan berbasis minyak bumi dan pelarut organik yang berbahaya. Temuan ini memberikan dasar untuk kemajuan lebih lanjut dalam teknologi resin berkelanjutan dan menawarkan potensi untuk implementasi skala industri.

UTILIZATION OF CRUDE GLYCEROL FROM BIODIESEL PRODUCTION FOR ULTRA-VIOLET CURABLE ALKYD RESIN PREPARATION VIA SOLVENT-FREE ENZYMATIC PROCESS

ABSTRACT

The development of environmentally friendly coatings has become a pressing necessity to address environmental concerns and regulatory restrictions on volatile organic compounds. This study explores a novel solvent-free enzymatic approach for synthesizing ultra-violet (UV) curable alkyd resin using biodiesel-derived crude glycerol, soybean oil, glycidyl methacrylate, itaconic anhydride, phthalic anhydride, and succinic anhydride. The synthesis process was optimized to maximize the yield of monoglycerides and enhance resin performance. First, the feasibility of using crude glycerol was confirmed through methanol and metal content analysis. Monoglycerides were then synthesized via solvent-free enzymatic glycerolysis, achieving a monoglyceride yield of 28.93% after reaction conditions were optimized using response surface methodology (RSM). Subsequently, a solvent-free system was employed for pre-reaction, enzymatic reaction, and UV curing, leading to the synthesis of UV curable alkyd resin films, resulting in a number-average molecular weight (M_n) of the resin of 1144 g/mol and a film gel content of 91.1% under preferred conditions. The properties of the UV-cured films were then evaluated. Increasing the molar ratio of succinic anhydride to phthalic anhydride improved the flexibility, adhesion, and impact resistance of the films but reduced hardness and contact angle, while solvent resistance remained stable. This study demonstrates that the integration of bioresources, a solvent-free enzymatic process, and UV curing enable the production of sustainable, high-performance, and environmentally friendly alkyd resins, reducing reliance on petroleum-based materials and hazardous organic solvents. The findings provide a foundation for further advancements in sustainable resin technology and offer potential for industrial-scale implementation.

CHAPTER 1

INTRODUCTION

1.1 Background

Alkyd resin, is a type of polyesters derived from polyols, polyacids, and oils (or fatty acids) (Kienle & Ferguson, 1929). This resin was first synthesized by Kienle in the mid-1920s which is favored for its low production cost and the superior properties of the film formed upon curing, where they account for approximately 28% of all resin usage (Eswaran, 2022). Despite their widespread use, the production and application of alkyd resin heavily rely on organic solvent as a dispersing agent, which is crucial for maintaining mixture uniformity and facilitating efficient heat dissipation during processing (Freitag & Stoye, 2008). This may also lead to the emission of volatile organic compounds (VOCs), many of which are toxic and harmful, posing significant environmental and health risks. However, due to the growing environmental awareness, stricter regulation on VOC emissions has been implemented (Tator & Koehler, 2015). In 1966, the United States introduced the first legislation to limit VOC emissions in coatings, mandating strict controls on solvent emissions during the drying process (Blank, 2001). Subsequently, other countries, including Japan, the United Kingdom, Germany, and China, have enacted similar restrictions on solvent-based alkyd resin. Since the 1960s, waterborne alkyd resin, which utilizes water as the primary dispersing agent, has gained prominence as a safer and more environmentally friendly alternative. These waterborne systems not only reduce production costs but also significantly lower VOC emissions, making them a key component in the development of eco-friendly coatings. However, waterborne alkyd resin faces limitations, including lower hardness, slower drying times, and reduced water and solvent resistance, which have constrained its application (Hofland, 2012). At the same time, with the continued depletion of petroleum resources and global warming, the coatings industry is shifting towards sustainable products (Dizman & Kaçakgil, 2023). One promising avenue is the development of bio-based UV curable resins, which combine solvent-free enzymatic synthesis with ultra-violet (UV) curing technology. This approach offers a viable solution to the limitations of traditional alkyd resin, paving the way for more sustainable and environmentally responsible coatings.

1.1.1 Solvent-free Enzymatic Synthesis Technology

The solvent-free enzymatic synthesis reaction is an environmentally friendly catalytic method with wide-ranging applications (Loos, 2022). Compared to the traditional synthesis of alkyd resin, it effectively addresses the cost and environmental pollution issues associated with solvents at the source (Pellis et al., 2015). Conventional alkyd resins undergo polycondensation at high temperatures (above 200 ℃), and organic solvents are usually added to reduce viscosity and facilitate the removal of small molecule by-products. Enzymatic synthesis occurs under mild conditions (below 100°C), minimizes side reactions (Gross et al., 2001). Additionally, lipases used as catalysts can synthesize polymers with special functions or unique structures that are challenging to achieve using conventional synthetic methods (Todea et al., 2021). Lipases are non-toxic, free from heavy metals, and the polyesters they synthesize exhibit excellent biodegradability and biocompatibility, making them applicable in various fields such as textiles, food, housing, and transportation (Lu et al., 2019). As a result, enzymatic catalysis is gaining increasing attention and has become a hot topic in recent research. The synthesis of polyesters under lipase catalysis can be accomplished through multiple pathways, including polycondensation, transesterification, and ring-opening reactions (Wang et al., 2022).

1.1.2 UV Curing Technology

UV curing has emerged as a high-efficiency, pollution-free technology characterized by its rapid film formation capabilities, often requiring merely seconds to fully cure coatings under UV exposure (Schwalm, 2006). Celebrated as a green industrial innovation for the 21st century, UV curing offers significant advantages over traditional thermal curing methods employed for alkyd resin. Notably, it eliminates the necessity for solvent-based resin dispersion, thereby substantially reducing the emission of VOCs associated with prolonged solvent evaporation during drying processes (Todorova et al., 2021). The benefits of UV curing are multifaceted, encompassing swift curing speeds, environmental friendliness, energy and cost savings, and versatility across a wide array of substrates. Furthermore, UV cured films are typically thinner yet exhibit superior performance characteristics, consuming less raw material in the process. The technology's compatibility with automation enhances operational efficiency, conserves space, and boosts production throughput (Javadi et al., 2016). In recent years, global research and application of UV curing technology have expanded markedly, solidifying its status as one of the most dynamic and rapidly advancing fields within the coatings industry (Liu et al., 2020).

1.1.3 UV Curable Alkyd Resin

UV curable alkyd resin is a specialized type of alkyd resin that, upon UV irradiation, triggers the opening and cross-linking of unsaturated double bonds, transforming a liquid into a solid state (Wang et al., 2023). These resins can be synthesized by reacting polyacids and polyols with UV-reactive functional groups. The raw materials used in UV curable alkyd resin include not only common compounds such as glycerol and phthalic anhydride but also unsaturated double bond-containing groups like unsaturated acids and anhydrides, acrylates, epoxy acrylates, and plant oil-based unsaturated fatty acid esters (Balgude & Sabnis, 2014; Fu et al., 2019; Ifijen et al., 2022; Patil et al., 2023). These materials are readily available, and the synthesis process is relatively simple, yielding cured films with excellent hardness, gloss, and heat resistance. UV curable alkyd resin is particularly advantageous in applications requiring rapid drying and low-temperature curing (Javadi et al., 2016). Moreover, by adjusting the proportion of raw materials, it is possible to synthesize UV curable alkyd resin with varying properties to meet diverse needs (Thanamongkollit et al., 2012).

1.1.4 Bio-based Materials for UV Curable Alkyd Resin

The raw materials used in UV curable alkyd resin can be derived from natural, renewable resources, aligning with the principles of sustainability. Given the non-renewable nature of petroleum resources and the environmental challenges posed by petroleum-based products, there is a growing interest in replacing petrochemical materials with bio-based alternatives (Harmsen et al., 2014; Weiss et al., 2012). Phthalic anhydride is one of the primary components in the synthesis of alkyd resin, and reducing its usage is consistent with sustainable development and environmental protection goals (Straathof & Bampouli, 2017). In recent years, the use of itaconic acid to produce bio-based UV curable resins has seen promising research and application in the coatings industry. Itaconic acid is one of the top 12 bio-based platform chemicals with significant potential for industrial use (de Jong et al., 2012). With its unsaturated double bonds and two carboxyl groups, itaconic acid exhibits reactive chemical properties. Substituting part of the phthalic anhydride in the resin with itaconic acid not only reduces dependence on petroleum resources but also introduces more double bonds, thereby enhancing the UV curing reactivity of alkyd resin (Brännström et al., 2017). Bio-based succinic acid, another of the top 12 bio-based platform chemicals, is an organic acid derived from renewable resources (de Jong et al., 2012). Modifying resins by partially replacing phthalic anhydride with succinic acid not only reduces petroleum usage but also improves the flexibility of the resin film (Dessie et al., 2023; Hevus et al., 2020). Glycerol, a key material in the synthesis of alkyd resin, is primarily sourced from fats and oils. With the advancement of the biodiesel industry, crude glycerol, a byproduct of biodiesel production, has become an inexpensive, continuously available, and growing bulk renewable bio-based material (Hejna et al., 2016). Notably, significant progress has been made in synthesizing alkyd resin from crude glycerol. Research has shown that the fatty acid esters in crude glycerol can be fully utilized, while other impurities can be removed through evaporation and precipitation during the synthesis of monoglycerides. The resulting alkyd resin based on crude glycerol exhibit excellent film-forming properties. The low cost and availability of crude glycerol make it a cost-effective alternative to refined glycerol, and its use is also significant for the sustainable development of UV curable alkyd resin (Wang et al., 2024).

1.2 Problem Statements

i. Crude glycerol is a by-product of biodiesel production. Although its main component is glycerol, it may contain impurities such as methanol and metal ions that inhibit enzyme activity. In addition, crude glycerol containing residual biodiesel components (such as fatty acid methyl esters, FAMEs) may affect the yield of monoglycerides. The feasibility of using crude glycerol for the enzymatic synthesis of monoglycerides remains to be further investigated.

ii. Although solvent-free enzymatic glycerolysis has been employed with various oils to produce monoglycerides (Palacios et al., 2022; Zou et al., 2020), the direct substitution of refined glycerol with crude glycerol has not been previously documented. The types of lipases and the specific reaction conditions for the solvent-free enzymatic synthesis of monoglycerides using crude glycerol remain unclear.

iii. Enzymatic synthesis is a highly effective tool in polymer synthesis. The enzymatic synthesis of itaconic acid polyesters, aliphatic polyesters, aromatic polyesters, and epoxy acrylate polyesters has been reported (Gryglewicz, 2003; Víctor Hevilla et al., 2021; Robert & Friebel, 2016; Varma et al., 2005; Wu et al., 1998). Unlike conventional polyesters, UV curable alkyd resin aims to achieve maximum UV cure rate rather than high degrees of polymerization or high viscosity (Lovell et al., 2001). Parameters such as enzyme concentration, reaction temperature and time, as well as photoinitiator concentration and UV exposure time during the curing process, can significantly influence the UV cure rate of the resin. The reaction conditions for the solvent-free enzymatic synthesis of UV curable alkyd resin using monoglycerides, phthalic anhydride, itaconic anhydride, and glycidyl methacrylate, as well as the optimal curing conditions, remain unclear.

iv. For the application of solvent-free enzymatically synthesized UV curable alkyd resin in the coatings industry, a comprehensive understanding of the coating film's performance characteristics is essential (Xu, 2017). The increase in succinic anhydride and the corresponding decrease in phthalic anhydride respectively leads to an increase in the linear aliphatic chains and a reduction in the aromatic ring structures within the resin, which in turn affect the film's properties (Abul Hasnat et al., 2024; Hayden et al., 2021). However, the performance attributes of UV cured alkyd resin films, such as water contact angle, hardness, flexibility, adhesion, impact resistance, and solvent resistance, at different succinic anhydride/phthalic anhydride ratios remain unclear.

This study combines renewable resources, solvent-free enzymatic synthesis, and UV curing technologies to develop a UV curable alkyd resin without the use of solvents, optimizing synthesis conditions and exploring the performance of the UV cured film. Initially, monoglycerides were synthesized by esterifying crude glycerol derived from biodiesel with soybean oil via transesterification process. The monoglycerides were then reacted with phthalic anhydride, itaconic anhydride, and glycidyl methacrylate to synthesize the UV curable alkyd resin. Building on this, a series of UV curable alkyd resins were synthesized by partially replacing phthalic anhydride with succinic anhydride. Finally, the UV curable alkyd resins were cured, and the performance of the resulting UV cured films was analyzed and evaluated. This research aims to contribute to the advancement of sustainable coating technologies by minimizing environmental impact while enhancing material properties.

1.3 Research Objectives (RO)

RO1. To analyze methanol, metal ion, biodiesel, and other impurity content of the crude glycerol to assess its suitability for the enzymatic synthesis of monoglycerides.

RO2. To synthesize monoglycerides from soybean oil and crude glycerol via solvent-free enzymatic process using different types of enzymes (Lipozyme RM IM, Lipozyme TL IM, and Novozym 435) at different reaction time, temperature, crude glycerol to oil ratio, and enzyme dosage.

RO3. To synthesize UV curable alkyd resin from different anhydride compounds (itaconic anhydride, phthalic anhydride, and succinic anhydride) via solvent-free enzymatic process at different ratios with predetermined conditions.

RO4. To investigate the properties of UV cured films with different succinic anhydride to phthalic anhydride ratios, including hardness, flexibility, adhesion, impact resistance, contact angle, and solvent resistance.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview of Alkyd Resin

In 1927, the concept of alkyd resin was introduced by General Electric Company in the United States, when a resin was synthesized by reacting glycerol with phthalic anhydride and unsaturated vegetable oils at high temperatures (Standeven, 2006). This marked the beginning of alkyd resin, which is a polyester resin formed through the polycondensation reaction of polyols and polyacids with vegetable oils or fatty acids. The advent of alkyd resin revolutionized the coatings industry, shifting it away from using drying oils and natural resins towards the era of chemically synthesized coatings. Over the nearly hundred years since their inception, alkyd resin has become a cornerstone in industrial coatings due to its widespread use. This prominence is largely attributable to the broad availability of raw materials, particularly the primary sources such as vegetable oils or fatty acids, which are natural and renewable resources (Dizman & Kaçakgil, 2023). These factors reduce costs and lessen the coatings industry's reliance on petrochemicals. Moreover, the cured alkyd resin film offers excellent adhesion, flexibility, gloss, and corrosion resistance. Through formulation adjustments, alkyd resin can be tailored into various products, including varnishes, enamels, lacquers, topcoats, primers, and putties (Müller & Schackmann, 2023; Poth, 2020).

2.1.1 Classification of Alkyd Resin

Alkyd resin can be classified primarily in two ways.

One method of classification is based on the type of vegetable oil or fatty acid used (Abul Hasnat et al., 2024):

i. Drying Oil Alkyd Resin: This alkyd resin is synthesized from vegetable oils or fatty acids with an iodine value greater than 140 g I_2/100g. Common drying oils include linseed oil, tung oil, and dehydrated castor oil. Alkyd resin made from these oils or fatty acids is characterized by fast drying times, high hardness, and high gloss, making it suitable for producing air-drying alkyd resin at room temperature (Kienle, 1949).

ii. Semi-Drying Oil Alkyd Resin: This alkyd resin is synthesized from vegetable oils or fatty acids with an iodine value ranging from 125 to 140 g I_2/100g. Common semi-drying oils include tall oil and soybean oil. Alkyd resin made from these oils tends to have slower drying times and is mainly used in the production of baking enamels. Although soybean oil is also a semi-drying oil, the alkyd resin made from it can still exhibit relatively good drying performance and is less prone to yellowing compared to resins made from drying oils like linseed oil and tung oil (Ahmed, 2024).

iii. Non-Drying Oil Alkyd Resin: This alkyd resin is synthesized from vegetable oils or fatty acids with an iodine value of less than 125 g I_2/100g. Examples include alkyd resin made from coconut oil, castor oil, and lauric acid. This alkyd resin dries extremely slowly and is primarily used in combination with amino resins to produce two-component amino-baking enamels. The resulting coatings have better hardness, alkali resistance, and durability compared to those made with single-component alkyd resin (Islam et al., 2014).

Alkyd resin can also be classified based on the proportion of plant oil or fatty acids in their formulation:

i. Long-oil Alkyd Resin: This resin contains more than 60% oil, providing excellent flexibility and flow properties. They are primarily used in outdoor coatings (Mutar & Hassan, 2017).

ii. Medium-oil Alkyd Resin: With an oil content ranging from 40% to 60%, this resin balance flexibility and hardness, making them widely applicable in industrial coatings (Rodríguez-Tobías et al., 2024).

iii. Short-oil Alkyd Resin: Containing less than 40% oil, this resin is characterized by higher hardness and are commonly used in baking enamels and industrial primers (Atimuttigul et al., 2006).

2.1.2 Composition and Structure of Alkyd Resin

Alkyd resin is a polymer formed through a polycondensation reaction involving three main components: polyols, polyacids or anhydrides, and fatty acids or vegetable oils. The main chain of the alkyd resin is composed of ester bonds, which are formed through the esterification reaction between polyols and polyacids. The length, rigidity, and degree of branching of the main chain determine the basic properties of the resin. For example, aromatic polyacids (such as phthalic anhydride) increase rigidity, while aliphatic polyacids (such as adipic acid) enhance flexibility (Falamarzpour et al., 2017; Luo et al., 1994). The side chains primarily originate from the polyol’s polyhydroxy structure and unsaturated fatty acids. The unsaturated bonds in fatty acids undergo auto-oxidation in the presence of air, forming peroxides, which initiate intermolecular cross-linking and lead to the curing of the resin into a film. This cross-linking reaction is fundamental to the curing process of alkyd resin. The side chains are also related to the drying speed and weather resistance of the coating film. For instance, highly unsaturated fatty acids contribute to faster drying, while saturated fatty acids enhance weather resistance (Lazzari & Chiantore, 1999; Long et al., 1968). Furthermore, by controlling the type, ratio, and degree of polymerization of the main chain and side chains, the viscosity, hardness, and film-forming properties of the resin can be adjusted. The choice and proportion of these components ultimately determine the final properties of the alkyd resin.

Polyols are a critical part of alkyd resin, providing the "backbone" structure of the resin (Tator & Koehler, 2015). Common polyols include glycerol and pentaerythritol.

Glycerol, also known as glycerin, is a simple polyol compound with the molecular formula $C_3H_8O_3$. Glycerol has a three-carbon linear structure, with no double bonds or other functional groups along the carbon chain. Each of the three hydroxyl groups is attached to one of the three carbon atoms, allowing glycerol to undergo esterification reactions with multiple acid groups, forming a three-dimensional network structure (Pagliaro et al., 2007). The absence of rigid or aromatic ring structures in glycerol's molecular structure typically results in resins with good flexibility (Ben et al., 2022). This flexibility is crucial for coatings that require elasticity or impact resistance. Additionally, the flexible molecular framework of glycerol helps balance the hardness and flexibility of the resin, ensuring that the coating film is rigid yet not overly brittle. Glycerol has high hydrophilicity due to its three hydroxyl groups, enhancing the water dispersibility and emulsifying properties of resins in waterborne formulations (Shi et al., 2015). This property aids in creating stable aqueous systems. Furthermore, glycerol's hydrophilic nature can improve hydration in coatings or adhesives that require some water solubility. Glycerol is derived from the hydrolysis or transesterification of animal and vegetable oil, making it a renewable resource (Ciriminna et al., 2014). In green chemistry and sustainable development, the use of glycerol reduces dependence on petroleum-based raw materials, lowering environmental impact.

Besides glycerol, pentaerythritol is an important tetrahydric alcohol with high functionality of its four hydroxyl groups that allows it to form more complex three-dimensional crosslinked networks (Shi et al., 2015). Resins made with pentaerythritol generally exhibit higher hardness, heat resistance, and corrosion resistance (Burrell, 1945). The tetrahydric structure of pentaerythritol provides uniform crosslinking, leading to better leveling during the curing process and contributing to the formation of smooth, even coating surfaces (Tang et al., 2020). This property makes pentaerythritol widely used in varnishes.

Polyacids or anhydrides react with polyols to form ester bonds, representing another critical component in alkyd resin (Chardon et al., 2021). Commonly used polyacids or anhydrides include phthalic anhydride and maleic anhydride. Phthalic anhydride is a typical anhydride with the molecular formula $C_8H_4O_3$. The molecule of phthalic anhydride contains a benzene ring, which imparts rigidity and stability to the molecule (Song et al., 2005). The two adjacent carbon atoms on the benzene ring each carry a carbonyl group, and these carbonyl groups are connected by an oxygen atom, forming an anhydride group. In alkyd resin, phthalic anhydride plays multiple essential roles due to its aromatic ring structure and the unique properties of the anhydride group. For example, resins containing phthalic anhydride exhibit higher hardness and rigidity, resulting in coatings with superior mechanical strength, abrasion resistance, and scratch resistance (Gogoi, 2015). Additionally, phthalic anhydride endows resins with excellent chemical resistance to acids, bases, and organic solvents, making alkyd resin suitable for industrial applications requiring chemically resistant coatings (PSCHORR, 1961). The aromatic ring structure of phthalic anhydride also enhances the thermal properties of the resin, providing good thermal stability at elevated temperatures. This makes alkyd resin containing phthalic anhydride ideal for baking finishes and heat-resistant coatings (Vlase et al., 2016). Moreover, the uniformity and stability of the phthalic anhydride structure help the resin form a smooth film surface during curing, making it widely used in high-gloss coatings and varnishes (Kienle & Ferguson, 1929). Phthalic anhydride is often employed to modify resins to enhance specific properties. For instance, phthalic anhydride can be copolymerized with maleic anhydride to adjust the resin's hardness, flexibility, and reactivity (Ahamad et al., 2001). In esterification reactions, phthalic anhydride acts as both a reactant and a catalyst, accelerating the synthesis of alkyd resin (Liu et al., 2014). Due to its wide range of applications and relatively economical production process, phthalic anhydride holds a vital position in the alkyd resin industry.

Maleic anhydride is an unsaturated organic compound with the molecular formula $C_4H_2O_3$. The molecule of maleic anhydride contains a carbon-carbon double bond and an anhydride group. Maleic anhydride plays a crucial role in the synthesis of alkyd resin (Trivedi, 2013). For instance, its double bond can copolymerize with other unsaturated monomers such as styrene or acrylates, improving the cross-linking and curing performance to create high-strength coatings (Rzaev et al., 1971). By copolymerizing with other monomers like phthalic anhydride, the hardness and flexibility of the final product can be adjusted to achieve a balance between these properties (Ahamad et al., 2001). The small molecular structure of maleic anhydride can reduce the viscosity of the resin system. When added to resin formulations, maleic anhydride can improve the leveling properties of the resin, leading to the formation of a smooth film surface and enhancing the final product's appearance quality (Wu et al., 2012). These characteristics make maleic anhydride a key ingredient in the coatings industry.

Succinic acid is a common aliphatic dicarboxylic acid that plays a crucial role in resin synthesis. Succinic acid contains two carboxyl groups, which react with polyols to form ester bonds, but its backbone is a straight-chain alkane structure, making it relatively soft and flexible. Compared to more rigid aromatic polyacids like phthalic anhydride, succinic acid provides greater molecular mobility, enhancing the flexibility and extensibility of the resin (Hevus et al., 2020). This characteristic makes resins containing succinic acid suitable for coatings that require higher flexibility and impact resistance. Due to its simple molecular structure and lack of rigid ring structures, the inclusion of succinic acid in a resin formulation tends to lower the overall hardness of the resin, making it appropriate for flexible coatings or elastomers (Pan & Webster, 2011). Additionally, succinic acid lacks unsaturated bonds, which contributes to the UV stability of alkyd resin containing succinic acid, reducing the likelihood of photodegradation and improving weather resistance in outdoor environments (Jirouš-Rajković & Miklečić, 2021). The combination of succinic acid with more rigid polyacids, such as phthalic anhydride, can achieve a balance between resin hardness and flexibility. For example, in certain coating formulations, the appropriate addition of succinic acid can reduce brittleness, enhance adhesion, and improve impact resistance, while still maintaining adequate hardness (Heinrich, 2017). Furthermore, succinic acid can be synthesized from renewable resources, such as through biotechnological fermentation processes, making it a potential green chemistry ingredient (Akash et al., 2023). In the context of sustainable development, the use of succinic acid as a resin component can reduce reliance on petroleum-based chemicals and lessen environmental impact.

Fatty acids or vegetable oils represent the third crucial component in alkyd resin, influencing the flexibility, drying speed, and weather resistance of the resin. Commonly used oils include linseed oil and soybean oil.

Linseed oil is a drying oil derived from plants, primarily composed of glycerides of various fatty acids. Its key fatty acid components include (Yang et al., 2021):

i. Alpha-linolenic acid, constituting approximately 55-60%, is an ω-3 polyunsaturated fatty acid with the molecular formula $C_{18}H_{30}O_2$, containing three double bonds,

ii. Linoleic acid, making up about 15-20%, is an ω-6 polyunsaturated fatty acid with the molecular formula $C_{18}H_{32}O_2$, containing two double bonds,

iii. Oleic acid, comprising roughly 15-20%, is a monounsaturated fatty acid with the molecular formula $C_{18}H_{34}O_2$, containing one double bond, and

iv. Saturated fatty acids, such as palmitic acid and stearic acid, account for about 5-10%.

In the synthesis of alkyd resin, linseed oil serves as a vital oil-based component, providing the resin with flexibility and excellent film-forming properties. The polyunsaturated fatty acids in linseed oil contain multiple double bonds, which, when exposed to air, undergo oxidative cross-linking reactions that cause the oil film to gradually cure. Linseed oil can dry at room temperature within a few hours to a few days, forming a robust coating, and its drying rate surpasses that of many other vegetable oils (de Viguerie et al., 2016). The cross-linked structure formed by linseed oil exhibits a certain degree of elasticity, enabling the coating to withstand deformation during use without cracking or peeling, making it suitable for architectural coatings. The oxidative cross-linking network formed during the drying process also imparts some UV and oxidative resistance, making linseed oil-containing coatings suitable for outdoor environments (Bansal et al., 2022). Linseed oil penetrates into the wood, filling the capillaries and forming a protective layer that prevents moisture and air from entering, thereby extending the lifespan of the substrate (Addis et al., 2020). The surface of wood treated with linseed oil takes on a natural sheen and warm tone (Brooks, 2021). By adjusting the oil content in the resin, the gloss and appearance can be tailored to meet different coating requirements. These properties make linseed oil a widely used and important material in modern industry.

Soybean oil is also a widely used vegetable oil, primarily composed of triglycerides derived from various fatty acids. The fatty acid composition of soybean oil mainly includes the following (Ivanov et al., 2010):

i. Linoleic acid, accounting for approximately 53%, is the major component of soybean oil. It is an ω-6 polyunsaturated fatty acid with the molecular formula $C_{18}H_{32}O_2$ and contains two double bonds,

ii. Oleic acid, constituting about 23%, is a monounsaturated fatty acid with the molecular formula $C_{18}H_{34}O_2$, containing one double bond,

iii. Linolenic acid, making up about 7-8%, is an ω-3 polyunsaturated fatty acid with the molecular formula $C_{18}H_{30}O_2$ and three double bonds,

iv. Palmitic acid, accounting for roughly 10%, is a saturated fatty acid with the molecular formula $C_{16}H_{32}O_2$, and

v. Stearic acid, comprising about 4%, is also a saturated fatty acid with the molecular formula $C_{18}H_{36}O_2$.

Soybean oil is classified as a semi-drying oil, which can undergo slow oxidative polymerization when exposed to air, resulting in limited oxidation and drying capabilities (Castro et al., 2006). During the preparation of alkyd resin, soybean oil serves as an oil-based component that can modulate the flexibility, water resistance, and gloss of the resin. Compared to other drying oils, soybean oil imparts better fluidity and processability to alkyd resin (Atimuttigul et al., 2006). The unsaturated fatty acids in soybean oil provide the resin with flexibility and plasticity, enhancing the impact and bending resistance of the coating during practical applications, reducing the likelihood of cracking (Salensky, 1946). The long-chain fatty acids in soybean oil contribute to improved water resistance of the resin or coating, particularly in high-humidity environments, helping to prevent moisture ingress and degradation of the film (Atimuttigul et al., 2006). Soybean oil is a natural, renewable vegetable oil. Its utilization in coatings and resins can reduce reliance on petrochemical-based materials, promoting the development of green chemistry (Schmitz et al., 2008). Due to its natural and safe properties, soybean oil exhibits good biocompatibility and is also used in food packaging coatings and medical coatings. Offering flexibility, water resistance, and environmental sustainability, soybean oil is a highly valuable raw material in the realm of vegetable oils.

2.1.3 Synthesis Mechanism of Alkyd Resin

The synthesis of alkyd resin primarily involves four key chemical reactions: esterification, transesterification, dehydration reactions, and addition reactions (Edens & Lochary, 2004).

Esterification refers to the reaction between the carboxyl groups of polyacids and the hydroxyl groups of polyols, resulting in the formation of ester bonds and the release of water. Due to the reversible nature of esterification, the presence of water as a by-product can shift the reaction equilibrium, hindering the complete conversion of reactants. If the water is not removed promptly, the reaction may reach equilibrium prematurely, preventing the full synthesis of the alkyd resin (Oil et al., 1993). The structure of the polyols and polyacids influences the reaction rate; for instance, pentaerythritol and trimethylolpropane, which contain multiple primary hydroxyl groups, exhibit higher reactivity with acids and require shorter reaction times compared to glycerol. When the polyacid is in the form of an anhydride, an exothermic half-esterification reaction occurs initially, characterized by high reactivity (Goldsmith, 1948). Subsequent esterification of the second carboxyl group with the hydroxyl group requires a higher temperature. Structurally, anhydrides such as maleic anhydride or phthalic anhydride react more favorably with polyols and at lower temperatures compared to isophthalic acid (Poth, 2020).

Transesterification involves the redistribution of ester groups between an oil and an excess of alcohol under heat and catalysis by acids or bases, resulting in the formation of a new ester and alcohol. This process is also known as alcoholysis and is a reversible reaction. Catalysts such as Lithium hydroxide or zinc oxide are typically used in alcoholysis, with reaction temperatures controlled between 210-250℃. The solubility increases when glycerol and oil are converted to monoglycerides, allowing the progression of the reaction to be monitored using the endpoint tolerance method (Nanvaee et al., 2013).

During the preparation of alkyd resin, dehydration reactions may occur between hydroxyl groups under high temperature conditions. This reaction tends to occur when polyhydroxy group monomers are used, leading to the formation of water and ethers. The number of hydroxyl groups decreases resulting in a slow decrease in acid value (Yin et al., 2014).

Addition reactions (Diels-Alder) can occur when unsaturated vegetable oil or unsaturated fatty acid, containing multiple double bonds or conjugated double bonds, is subjected to heat. These reactions may vary in degree depending on the conditions. Additionally, during the synthesis of alkyd resin, exposure to oxygen at high temperatures can lead to significant side reactions, darkening the resin and potentially causing gelation of the system. Therefore, it is critical to strictly isolate the reaction from oxygen during the preparation process (Oil et al., 1993).

In summary, the synthesis of alkyd resin is a complex, multi-step process, with the underlying mechanism driven by the stepwise esterification reactions between hydroxyl and carboxyl groups, leading to the formation of high molecular weight polyester chains. The process typically begins with either esterification or transesterification. As the reaction progresses, low-molecular-weight products continue to react with free polyols and polyacids, resulting in chain growth. When the alkyd resin reaches the desired molecular weight and viscosity, the reaction is terminated by cooling or by adding terminators such as amines or polyols. By meticulously controlling the synthesis process, alkyd resin with various performance characteristics can be produced to meet a wide range of industrial applications (Lin, 2000).

2.1.4 Synthesis Methods of Alkyd Resin

Alkyd resin is a polymer formed by the condensation polymerization of polyacids, polyols, and vegetable oils or fatty acids. When fatty acids are used as the starting materials, all the reactants can be added directly into the reactor for the synthesis. However, when vegetable oil is used, the one-step addition method cannot be employed due to the immiscibility of vegetable oil with polyol and polyacid. Instead, the vegetable oil must first undergo high-temperature alcoholysis with polyol before other reactants are added. Otherwise, the poor solubility of vegetable oil in polyacid and polyol would result in a biphasic system, significantly slowing down the reaction. The main synthesis methods for alkyd resin are the fatty acid method and the alcoholysis method (Kaska & Lešek, 1991; Lin, 2000).

The fatty acid method is employed when fatty acids are used as raw materials (Aghaie et al., 2012; Murillo et al., 2010). The advantages and disadvantages of the fatty acid method are shown in Table 2.1. Since fatty acids are miscible with polyol and polyacid, the process can be carried out in a one-step addition manner. Typically, all reactants are added to the reactor at once, and the mixture is heated while stirring until the reaction temperature reaches 200-250°C. The reaction proceeds until the acid value and viscosity meet the required specifications, after which the reaction is stopped, cooled, and the product is diluted and filtered. In theory, due to the occurrence of transesterification reactions, the final product should reach a relative equilibrium regardless of the order of addition of the reactants. However, in practice, this is not the case. The reactivity of the hydroxyl group on different positions of the polyol molecule and the carboxyl group on different positions of the polyacid molecule varies, and the transesterification reaction between the formed ester intermediate occur very slowly. Therefore, the structure of the final product differs depending on the order of addition of the reactants. Kraft (Kraft, 1962) proposed the polymerization method for producing alkyd resin, where all the polyols, polyacids, and a portion of the fatty acid are first reacted to form a polymer with a certain molecular weight. The remaining fatty acids are then added to the reactor, and the reaction proceeds until the acid value meets the required specifications. Alkyd resin prepared by this method tends to have a lighter color, improved drying properties, and enhanced alkali resistance, although the viscosity may be relatively higher.

Table 2.1 Advantages and disadvantage of the Fatty Acid Method (Hadzich et al., 2020; Hovey, 1949)

No.	Advantages	Disadvantage
1	The absence of glycerol in fatty acids allows to produce glycerol-free alkyd resin	The cost of fatty acid is higher than that of oil
2	Both one-step and stepwise addition methods can be used	Fatty acid is corrosive, requiring more stringent equipment
3	Fatty acid can be further refined to select for a higher iodine value and lighter color, enabling the production of lighter-colored, better-drying alkyd resin	Fatty acid must be stored in sealed containers to prevent oxidation and darkening

The alcoholysis method is employed when oil is used as raw materials in the making of alkyd resin (Islam et al., 2014; Kumar et al., 2010). The advantages and disadvantages of the fatty acid method are shown in Table 2.2. Due to the immiscibility of oil with polyol and polyacid during the reaction, the system becomes biphasic, causing the reaction to proceed very slowly. The alcoholysis method involves the transesterification of oil with an excess of polyol under the influence of a catalyst and heat, resulting in the formation of partial glycerides. Once the ethanol tolerance of the system reaches the required level, polyacid is added, and the temperature is raised to 200-250°C for the esterification reaction, which is similar with the fatty acid method.

Table 2.2 Advantages and disadvantage of the Alcoholysis Method (Chiplunkar & Pratap, 2016; Hlaing & Oo, 2008; Resins, 1998)

No.	Advantages	Disadvantage
1	Can utilizes renewable and abundant natural oils, such as soybean oil and linseed oil, aligning with sustainable development goals	The reaction typically requires a long time, affecting production efficiency
2	Can maximizes the utilization of triglycerides in oils, reducing waste	The process may generate free fatty acid and other by-products, necessitating further treatment
3	Allow for flexible adjustment of the alkyd resin’s properties by varying the ratio of polyols to oils, meeting different application needs	The natural oil used in the alcoholysis method has complex and variable compositions, making it difficult to achieve consistent product performance across different batches

During the synthesis of alkyd resin, whether by the fatty acid method or the alcoholysis method, it is essential to remove the water produced during the reaction (Oil et al., 1993). The melt method, although commonly used, tends to result in products with darker colors, significant material losses, and lower quality. In contrast, the solvent method yields alkyd resin with lighter colors, reduced material loss, and higher product yields, and it allows for better temperature control. The solvent method was developed as an improvement over the melt method, utilizing organic solvent as a azeotropic agent to carry away the water generated by the esterification reaction. Typically, 3-5% of xylene is added for azeotropic dehydration (Nelson, 2012). When fatty acid is used as the raw material, xylene is added to the reactor along with the polyacid, polyol, and fatty acid at the start of the reaction. However, when vegetable oil is used as the raw material, xylene is added to the reactor along with the polyacid after the alcoholysis reaction is complete. The reaction temperature in the solvent method is easier to be controlled compared to the melt method, and it can be regulated by adjusting the amount of azeotropic solvent added. If the refluxing solvent is too high, it will carry back too much water, which can inhibit the esterification reaction. Conversely, if the temperature is too low, polyacid such as phthalic anhydride or isophthalic acid can be dissolved in the xylene may precipitate and crystallize, leading to blockages in the pipelines (Oil et al., 1993).

2.1.5 Curing Mechanism of Alkyd Resin

The curing of alkyd resin follows an auto-oxidation mechanism (Wei et al., 2013). During the drying and film formation process of alkyd resin, two primary film formation methods are involved: physical and chemical. As shown in Figure 2.1, these drying processes occur simultaneously. Initially, physical drying plays a dominant role, primarily driven by the evaporation of solvents. The drying rate at this stage is mainly determined by the vapor pressure of the solvent. As the solvent evaporates, the viscosity of the coating film increases, restricting the solvent's diffusion from the bottom layer to the surface, thereby slowing down the evaporation rate. Subsequently, chemical drying becomes the dominant process. The unsaturated double bonds in the vegetable oil or fatty acid undergo reactions with oxygen to form hydroperoxide compounds. These hydroperoxide compounds then decompose into alkyl radical, which follow the mechanism of free radical polymerization to form a cross-linked network of macromolecules (Bartolozzi et al., 2014). The cross-linking squeezes out solvent molecules trapped in the molecular chain gaps, facilitating their evaporation (Erich et al., 2005; Erich et al., 2006). The drying speed of alkyd resin largely depends on the type of vegetable oil or fatty acid used, the temperature and humidity of the