PREPARATION AND CHARACTERIZATION OF UV-CURABLE SOLVENT-FREE COATINGS DERIVED FROM NEEM OIL AND THEIR APPLICATIONS AS FLAME RETARDANT AND TERMITE ANTIFEEDANT

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by

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LIST OF ABBREVIATIONS

AESO	Acrylic epoxide soybean oil
AHP	Aluminium ammonium phosphinate
ATH	Aluminium hydroxide
ASTM	American Society for Testing and Materials
BPO	Benzoyl peroxide
COMA	Castor oil maleic anhydride
CMC	Carboxymethylcellulose
CS	Chitosan
CLEO	Curry leaf essential oil
CSPI	Cotton seed protein isolate
DTG	Derivatives of thermogravimetric analysis
DAP	Diammonium phosphate
DAMA	Dopamine methacrylamide
DAPB	Dially-4-phenylphophonic benzoic
DA	Dially
DOPO	10-Dihydro-a-oxa-10-phosphaphenanthrene-10-oxide
DMMP	Dimethyl methylphosphonate
u-EDC	Micro electric discharge
EUG@CMC-PGMA-CS	Eugenol-loaded nano delivery system
ESO	Epoxide soya bean oil
ESI-MS	Electrons pray ionization mass spectroscopy
FTIR	Fourier transform infrared spectroscopy
FAF	Flavorings applied food
TGA	Thermogravimetric Analysis
GMA	Glycidyl methacrylate

1H NMR	Proton nuclear magnetic resonance
HTP-FR	Hydroxy triazole phosphorus-containing reactive flame retardant
H_3PO_4	Phosphoric acid
IA	Itaconic acid
IRGACURE	1800 Hydroxy-cyclohexyl-ketone
ICP-OES	inductively coupled plasma optical emission spectroscopy
K_2HPO_4	Potassium hydrogen phosphate
Mel	Melamine
MEK-P	Methylethylketone peroxide
MAP	Mono ammonium phosphate
MEK	Methylethylketone solvent
Mw	Molecular weight
MDH	Magnesium hydroxide
MG	Monoglyceride
NO	Neem oil
NOB	Neem oil-based coating
NPK	Nitrogen Phosphorous Potassium
PA	Phosphoric acid
PMI	Polymethacrylimide
PER	Pentaerythritol
PPG	Polypropylene glycol
PEG	Polyethylene glycol
PDMS	Polydimethylsiloxane
SCPUA	Soy-castor oil-based polyurethane acrylate
SBC	Soybean based- Coating
STMP	Trimetaphosphate

TAEP	Tri(acryloyloxyethyl) phosphate
TiO_2	Titanium(iv)oxide
TnBP	Tri-n-butylphophate
UV	Ultraviolet
VOC	Volatile organic carbon
VMDMS	Vinyl methyl dimethoxy silane
$Zn_3(PO_4)_2.4H_2O$	Zinc phosphate tetrahydrate

PENYEDIAAN DAN PENCIRIAN PENGLITUP BEBAS PELARUT TERMATANG UV BERASASKAN MINYAK NEEM DAN PENGGUNAAN KALIS API DAN ANTI MAKAN ANAI-ANAI

ABSTRAK

Kajian ini membentangkan pembangunan bahan salutan bifungsi yang boleh disembuhkan UV dan bebas pelarut yang berasal dari minyak neem, direka dengan sifat kalis api dan anti makan anai-anai. Salutan berasaskan petroleum konvensional sering mengandungi sebatian organik meruap (VOC), yang menimbulkan bahaya besar terhadap alam sekitar dan kesihatan. Sebagai alternatif, minyak neem menawarkan sumber bio yang lestari kerana kandungan trigliseridanya yang tinggi dan bioaktiviti semula jadi. Walau bagaimanapun, sifatnya yang tidak kering mengehadkan aplikasinya dalam sistem bebas pelarut. Kajian ini bertujuan untuk mengatasi had ini dengan mengubahsuai kimia minyak neem menggunakan asid fosforik sebagai monomer silang dan agen penahan api, untuk menghasilkan salutan yang tahan lama dan multifungsi. Metodologi yang digunakan melibatkan transesterifikasi minyak neem dengan nisbah gliserol-ke-minyak yang berbeza (1.6:1 hingga 2.4:1, berdasarkan berat ekuivalen) untuk mendapatkan campuran mono-, di-, dan trigliserida melalui tindak balas alkoholisis pada suhu 220–230 °C selama dua jam. Intermediari yang dihasilkan kemudian direaksikan dengan asid itakonik dan glisidil metakrilat (nisbah molar 1:1) dengan kehadiran kepekatan asid fosforik yang berbeza untuk membentuk resin polimer. Resin yang terhasil kemudiannya dicampurkan dengan 3% Irgacure 184 sebagai pemula foto dan disembuhkan di bawah sinaran UV dengan kelajuan penghantar 5 m/min selama 10 kitaran untuk menghasilkan filem salutan pepejal. Intermediari dan resin dicirikan melalui penentuan nilai hidroksil dan kromatografi gas

(GC), manakala berat molekul dan pengenalan kumpulan berfungsi dilakukan menggunakan analisis viskometri dan FT-IR, masing-masing. Prestasi salutan dinilai melalui pengukuran kandungan gel, kekerasan pendulum, pelekat silang, kekuatan tarik keluar, dan ujian ketahanan impak. Sifat terma dan penahan api dianalisis menggunakan analisis termogravimetri (TGA), ujian api metanamina, dan piawaian pembakaran menegak UL-94. Ketahanan terhadap anai-anai salutan dinilai menggunakan ujian anti-pemakanan, ujian penolakan arena, dan penilaian toksikologi melalui eksperimen daya sentuhan. Keputusan menunjukkan peningkatan progresif dalam kandungan monogliserida (14.83% hingga 34.20%) dengan peningkatan nisbah gliserol, manakala digliserida kekal stabil dan trigliserida menurun. Nilai hidroksil dan berat molekul meningkat dengan kandungan gliserol dan asid fosforik. Spektrofotometri UV-Visible mengesahkan Irgacure 184 sebagai pemula foto yang sesuai. Salutan menunjukkan kandungan gel yang sangat baik (>95%) dan integriti mekanikal, tanpa retakan yang dilihat pada ketinggian impak 25 inci dalam sampel PA yang tinggi. Kekuatan tarik keluar dan kekerasan permukaan bertambah dengan peningkatan kepekatan PA, yang dikaitkan dengan peningkatan penyilangan. Salutan dengan kandungan PA yang lebih tinggi juga menunjukkan kebolehan basah yang berkurangan dan kekerasan pendulum yang lebih tinggi. Keputusan TGA mengesahkan kestabilan termal yang dipertingkatkan dan hasil char yang lebih tinggi dengan peningkatan PA, yang berkait rapat dengan peningkatan ketahanan api. Ujian metanamina menunjukkan pengurangan dalam penyebaran api dari 3.7 cm (0.4% PA) kepada 2.4 cm (2.0% PA), manakala penarafan UL-94 meningkat dari V-1 kepada V-0. Salutan menunjukkan kesan anti-pemakanan yang kuat terhadap termite dengan kadar kematian yang tinggi dalam kalangan pekerja dan kadar penggunaan yang berkurangan dalam sampel yang disalut, walaupun penolakan dan toksikologi yang

terhad diperhatikan. Kesimpulannya, salutan berasaskan minyak neem yang boleh disembuhkan UV dan bebas pelarut telah berjaya disintesis dengan fungsi dwifungsi sebagai penahan api dan anti-termite. Kajian ini menunjukkan potensi minyak neem sebagai bahan mentah lestari untuk teknologi salutan mesra alam, menawarkan alternatif yang berdaya maju kepada sistem berasaskan pelarut konvensional.

PREPARATION AND CHARACTERIZATION OF UV-CURABLE SOLVENT-FREE COATINGS DERIVED FROM NEEM OIL AND THEIR APPLICATIONS AS FLAME RETARDANT AND TERMITE ANTIFEEDANT

ABSTRACT

This research presents the development of a UV-curable, solvent-free bifunctional coating material derived from neem oil, designed with both flame-retardant and anti-termite properties. Conventional petroleum-based coatings often contain volatile organic compounds (VOCs), posing significant environmental and health hazards. As an alternative, neem oil offers a sustainable, bio-based resource due to its high triglyceride content and inherent bioactivity. However, its non-drying nature limits its application in solvent-free systems. This study aims to overcome this limitation by chemically modifying neem oil with phosphoric acid as a crosslinking monomer and flame-retardant agent, to produce a durable, multifunctional coating. The methodology involved the transesterification of neem oil with varying glycerol-to-oil ratios (1.6:1 to 2.4:1, on an equivalent weight basis) to obtain a mixture of mono-, di-, and triglycerides using an alcoholysis reaction at 220–230 °C for two hours. The resulting intermediates were reacted with itaconic acid and glycidyl methacrylate (1:1 molar ratio) in the presence of varying concentrations of phosphoric acid to form polymeric resins. The resins were then mixed with 3% Irgacure 184 photo initiator and cured under UV irradiation at a conveyor speed of 5 m/min for 10 cycles to obtain solid coating films. The intermediates and resins were characterized through hydroxyl value determination and gas chromatography (GC), while molecular weight and functional group identification were performed using viscometry analysis and FT-IR, respectively. Coating performance was evaluated through gel content measurement, pendulum hardness, cross-hatch adhesion, pull-off strength, and impact resistance tests. Thermal and flame-retardant properties were analysed using thermogravimetric analysis (TGA), methenamine flame tests, and the UL-94 vertical burning standard. The termite resistance of the coatings was assessed using anti-feeding assays, arena repellence tests, and toxicity evaluations through force-to-contact experiments. Results showed a progressive increase in monoglyceride content (14.83% to 34.20%) with increasing glycerol ratios, while diglycerides remained relatively stable and triglycerides declined. Hydroxyl values and molecular weights increased with both glycerol and phosphoric acid content. UV-Visible spectrophotometry confirmed Irgacure 184 as the suitable photo initiator. The coatings exhibited excellent gel content (>95%) and mechanical integrity, with no cracks observed at 25-inch impact height in high PA samples. Pull-off strength and surface hardness improved with PA concentration, attributed to enhanced crosslinking. Coatings with higher PA content also demonstrated reduced wettability and higher pendulum hardness. TGA results confirmed improved thermal stability and higher char yield with increasing PA, correlating with enhanced flame retardancy. Methenamine tests showed a reduction in flame spread from 3.7 cm (0.4% PA) to 2.4 cm (2.0% PA), while UL-94 ratings improved from V-1 to V-0. The coatings exhibited strong anti-feeding effects against termites with high mortality among the workers and reduced rate of consumptions among the coated samples, although limited repellences and toxicity were observed. In conclusion, a UV-curable, solvent-free neem oil-based coating was successfully synthesized with dual flame-retardant and anti-termite functionalities. The study demonstrates the potential of neem oil as a sustainable raw material for eco-friendly

coating technologies, offering a viable alternative to conventional solvent-based systems.

CHAPTER 1

INTRODUCTION

1.1 Overview of the Research

The necessity for environmentally friendly raw materials in the resin business has highlighted the importance of sustainability. Paints, coatings, and other industries frequently use renewable resin, a polymer made with mostly vegetable oils as a raw ingredient[1]. Vegetable oil has several benefits, including being a sustainable, biodegradable, and ecofriendly energy source for industry. These attributes have become crucial factors for the coating industries in recent years[2].

Wood-based materials are widely used in construction, furniture, and packaging due to their availability, renewability, and aesthetic appeal. However, their vulnerability to environmental factors such as moisture, microbial attack, insect infestation, and fire has necessitated the use of protective coatings[3,4]. Traditional wood coatings are predominantly solvent-based, containing significant amounts of volatile organic compounds (VOCs) that evaporate during the drying and curing processes[5,6]. These VOCs pose serious environmental and health hazards, contributing to air pollution and increasing the risk of respiratory illnesses, neurological disorders, and certain cancers[7]. Furthermore, the emission of VOCs plays a significant role in the formation of ground-level ozone and photochemical smog, prompting global environmental and public health concerns[8].

In response to these issues, the coating industry is shifting toward sustainable alternatives that minimize environmental impact and health risks. Bio-based coatings, derived from renewable raw materials, have attracted considerable attention as eco-friendly options[9]. Vegetable oils such as linseed, soybean, and neem oil have emerged as promising candidates due to their abundance, biodegradability, and chemical modifiability. Among these, neem oil is particularly suitable for wood protection applications because of its natural insect-repellent and antimicrobial properties. Neem oil contains long-chain triglycerides, allowing chemical modification for polymeric coating synthesis[10].

To further support sustainability, UV-curable coating systems have gained attention due to their rapid curing under ambient conditions, low energy requirements, and elimination of solvent emissions. These systems rely on photoinitiated polymerization, which produces crosslinked networks upon exposure to ultraviolet light without the need for thermal curing or solvent evaporation. UV-curable formulations offer reduced processing time and improved environmental performance, making them suitable for high-efficiency, solvent-free coatings[11-13]. Also, in order to enhance the UV curability of the coating material, itaconic and GMA was introduced in (1:1 ratio) to add unsaturated groups and make it UV curable film.

Despite the advantages of bio-based and UV-curable systems as previously mentioned in this research, one major challenge remains the lack of intrinsic flame resistance in most vegetable oil-derived coatings. This limitation restricts their applicability in fire-prone environments or structural wood applications. To overcome this, flame-retardant additives must be integrated into the coating formulation. However, many commercial flame retardants are halogen-based and associated with toxicity, environmental persistence, and bioaccumulation[14]. In this regard, Phosphorus-based compounds, such as phosphoric acid, have emerged as safer, more effective flame-retardant alternatives and preferred non-halogenated that promote char formation and reduce smoke generation during combustion, as in the case of this study based on relevant literature as discussed in the subsequent paragraph.

Phosphoric acid and its derivatives, such as phosphate esters, are preferred non-halogenated flame retardants in coatings due to their effective char-forming mechanism, which creates a thermally insulating barrier to suppress combustion[15]. This outperforms alternatives like melamine, which relies on gas dilution, or metal hydroxides, which require high loadings (40–60 wt.%) that compromise coating properties[16-18].

Phosphoric acid offers excellent compatibility with coating resins, ensuring uniform distribution without affecting aesthetics, unlike ammonium polyphosphate (APP), which can cause opacity or sedimentation, or metal hydroxides, which increase viscosity[19]. Its synergistic role in intumescent systems, combined with carbon sources and blowing agents, enhances fire resistance at lower concentrations, preserving coating flexibility and adhesion[19]. Phosphate based-coating from guanidine phosphate, thermal stability supports its use in high-temperature processing, unlike borates, which may degrade[20]. It also has a favourable toxicological profile, avoiding harmful byproducts like cyanuric acid from melamine[21] and lower environmental impact than resource-intensive metal hydroxides[16]. Cost-effective and widely available compared to nano-clays [22]. Therefore, phosphoric acid is ideal for large-scale applications. However, formulation-specific factors, such as substrate and environmental exposure, must be optimized for performance.

The present study seeks to address this gap by developing a novel, solvent-free application, UV-curable neem oil-based coating system with dual functionality of flame retardancy and termite resistance. The research involves the chemical modification of neem oil and the incorporation of phosphoric acid as a reactive monomer. By optimizing the formulation parameters, particularly the phosphoric acid content and the glycerol to neem oil (G:NO) ratio, the study aims to enhance thermal stability, adhesion, and fire performance of the coating while maintaining its biological protective functions. This approach not only eliminates harmful VOC emissions but also contributes to material innovation and sustainability.

Ultimately, this research aligns with the goals of green chemistry and supports the United Nations Sustainable Development Goals (SDGs), particularly **SDG 9** (Industry, Innovation, and Infrastructure) and **SDG 12** (Responsible Consumption and Production). It addresses a critical need for multifunctional coatings (flame retardant and anti-termites) that are both environmentally responsible and technically robust, contributing to safer and more sustainable wood protection strategies.

1.2 Statement of the Problems

In response to increasing regulatory and environmental pressures, there is growing interest in the development of eco-friendly, bio-based coatings with dual functionalities that eliminate the use of harmful solvents-based coatings formulated with volatile organic compounds (VOCs) while maintaining or enhancing mechanical and protective properties[23-25].

Neem oil, derived from the seeds of *Azadirachta indica*, is a renewable, biodegradable natural resource rich in triglycerides and biologically active compounds. Its inherent insecticidal and antimicrobial properties make it a promising candidate for sustainable coating applications[26]. However, neem oil's non-drying nature and poor film-forming behaviours pose challenges to its use in solvent-free and

UV-curable systems. Moreover, its application in multifunctional coatings that combine flame retardancy and termite resistance remains insufficiently studied.

Fire safety is a major concern in wood-based construction and furniture, where materials are inherently flammable. Although halogenated and phosphorus-based flame retardants are effective in reducing combustibility, they are often associated with ecological toxicity, poor biodegradability, and increasing regulatory restrictions[27]. While neem oil contains compounds such as azadirachtin and nimbin[26], their role in enhancing thermal stability and flame retardancy of coatings is yet to be systematically investigated and improve, particularly in a solvent-free application and UV-curable technology.

Equally, the problem of termite infestation, which significantly undermines the structural integrity of wooden materials, leading to costly damage globally. Although synthetic pesticides and preservatives such as chlorinated hydrocarbons and borates are effective, they pose long-term risks to human health and the environment[28]. Neem oil has long been recognized for its anti-feeding effects against termites, yet its incorporation into functional coatings to provide durable protection under real-world conditions remains underdeveloped and limited research is done on it.

Volatile organic compounds (VOCs) released during paint drying pose serious health risks. They contribute to ozone formation, a harmful air pollutant. Short-term exposure can cause headaches, skin irritation, and respiratory problems. Long-term exposure is linked to a higher cancer risk, especially lung cancer, with a 20–40% increase reported by the WHO[29].

UV-curable technology offers a promising solution, particularly when integrated with renewable resources, as it eliminates the need for organic solvents and enables rapid, energy-efficient curing at ambient temperature. Moreover, UV-curable renewable coatings provide enhanced film properties such as improved hardness, chemical resistance, and adhesion, while significantly reducing carbon footprint and production time. However, the adoption of such systems remains limited by formulation challenges, particularly when utilizing non-drying bio-based oils like neem oil, which require chemical modification to achieve adequate crosslinking and performance. Addressing these limitations is crucial to advancing sustainable, high-performance coatings that comply with environmental regulations and meet industrial demands. These gaps in practical utilization and performance evaluation hinder the broader adoption of neem oil as a viable green alternative in the coatings industry.

Therefore, there exists a clear need to develop a green, solvent-free coating system that integrates both flame-retardant and termite-resistant functionalities. Addressing this problem requires an in-depth understanding of neem oil chemical modification, its compatibility with flame-retardant monomers such as phosphoric acid, and the formulation of UV-curable systems capable of delivering long-term performance. This study aims to bridge these knowledge and application gaps by formulating and characterizing a neem oil-based, multifunctional coating, offering a sustainable and non-toxic alternative to conventional coatings reliant on petrochemicals and hazardous additives. This research will help in achieving Sustainable Development Goals of sustainable cities and communities, responsible consumption and productions, industry, innovation and infrastructure.

1.3 Research Objectives (RO)

RO1. To develop a UV-curable and insect-repellent coating by utilizing neem oil (NO) as a sustainable raw material, highlighting its natural bioactive properties.

RO2. To incorporate phosphoric acid as a flame-retardant monomer in the synthesis of UV-curable neem oil-based resins and to investigate its optimal content and the effect of PA: (G:NO) ratios on the resin's thermal stability, flame resistance, mechanical strength and adhesion strength, with the goal of achieving dual-functional coatings for improve rubber wood protection against fire damage and termite attack.

RO3. To evaluate the synthesized coating for its insect-repellent, antifeedant, and toxicity effects, as well as to assess its flame-retardant properties under varying phosphoric acid content to G:NO ratios using equivalent weight basis.

1.4 Scope and Limitations of the Research

This research is focus on the development and evaluation of a solvent-free application, UV-curable neem oil-based coating system specifically formulated for dual protection of rubber wood against flame and termite attack. The study involves the chemical modification of neem oil, a renewable and biodegradable resource, to create a sustainable polymeric backbone suitable for coating applications. A key feature of the formulation is the incorporation of phosphoric acid as a reactive monomer, aimed at imparting flame-retardant characteristics to the coating without the use of halogenated compounds.

The scope further includes the systematic optimization of formulation parameters, particularly the PA (0.4 to 2.0) and the glycerol 1.6 to 2.4 (G:NO) ratio, to enhance the thermal stability, flame resistance, and adhesion strength of the resin cured film.

The synthesized coating is applied to rubber wood substrates, and its performance was thoroughly evaluated using a range of characterization techniques, including Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), mechanical testing, and contact angle measurement. Biological efficacy was assessed through standardized antifeeding, repellences and toxicity bioassays against *Coptotermes* species only, providing insight into the termite-resistance behaviour of the coating. The research also contributes to the field of sustainable materials by addressing environmental and performance challenges associated with conventional solvent-based coatings.

1.5 Limitation of the Research

Despite the promising objectives and outcomes, the research was subject to several limitations that define its boundaries. Firstly, the synthesis and testing of the coatings are confined to laboratory-scale procedures, and no pilot or industrial-scale production is undertaken. As a result, scalability and industrial applicability are not directly addressed.

Secondly, the application of the developed coating is limited to rubber wood, chosen for its relevance in tropical construction and furniture industries. However, the performance of the coating on other wood species or composite materials remains unexamined. Also, soybean was selected for comparison due to its commonly used in making resin, versatility, semi-drying nature and its resin was prepared under control condition in the laboratory and devoid of solvent.

Another limitation involves the environmental testing conditions. The study does not include long-term weathering, UV exposure, or humidity cycling to simulate aging and environmental degradation, which are critical factors for assessing real-world durability. Similarly, fire resistance testing is conducted under controlled conditions and may not accurately reflect field performance in diverse fire scenarios.

Finally, the biological assessment of termite resistance is restricted to the *Coptotermes* genus, and the coating's effectiveness against other termite species or wood-boring insects is not investigated. Also, the validation of the neem oil-based coating was only limited to soybean-based coating. Due to its commonly used in making resin, versatility, semi-drying nature and its resin was prepared under control condition in the laboratory and devoid of solvent. However no direct comparison with any commercial products.

These limitations suggest directions for future research to broaden the applicability and reliability of the developed coating system.

CHAPTER 2

LITERATURE REVIEW

2.1 Bio-Based Coatings Development

The escalating environmental concerns surrounding volatile organic compounds (VOCs) and the depletion of fossil resources have catalysed the development of sustainable alternatives in the coatings industry. Bio-based coatings derived from renewable resources such as plant oils, proteins, and polysaccharides, offer a viable pathway to reduce environmental impact while meeting stringent regulatory standards. These coatings leverage agricultural and waste-derived feedstocks to create eco-friendly solutions with applications spanning automotive, construction, packaging, and medical sectors[30]. This subsection explores recent advancements in bio-based coating technologies, their applications, market trends, and the challenges impeding their widespread adoption.

Significant progress has been made in the formulation of bio-based coatings with innovations in material composition driving performance improvements. Bio-based polyurethane coatings synthesized from soybean, castor or linseed oils, exhibit excellent durability, chemical resistance and flexibility, making them suitable for high-performance applications[31,32]. Recent developments include hybrid systems combining bio-based polyols with conventional isocyanates and the exploration of non-isocyanate polyurethanes to mitigate health risks associated with isocyanate exposure. Similarly, bio-based powder coatings, utilizing binder systems such as poly(limonene carbonates) and polyester resins, offer zero VOC emissions, high recyclability, and low toxicity, aligning with circular economy principles[33,34]. In the realm of barrier coatings for food packaging, modified nanocellulose, lignin nanoparticles and bio-polyesters provide effective resistance to grease, oxygen, and moisture with chitosan-based coatings introducing antimicrobial properties for edible applications[35,36]. Additionally, epoxidized vegetable oils (EVOs) have emerged as a cost-effective biodegradable alternative for epoxy coatings with tenable thermomechanical properties that cater to diverse industrial needs[37].

Beyond material innovation, bio-based coatings are being engineered with advanced functionalities to address specific industrial requirements. For instance, chitosan and polybenzoxazine coatings derived from L-tyrosine demonstrate antimicrobial and antifouling properties, making them ideal for medical devices and marine applications[38]. Hydrophobic coatings based on starch and nanocellulose are replacing polyfluoroalkyl substances (PFAS) in textiles and packaging, offering grease resistance and waterproofing. Moreover, bio-based coatings are being tailored for high-performance applications, such as anticorrosion and fire-resistant coatings for aerospace and automotive industries, showcasing their versatility in demanding environments[39]. These functional advancements underscore the potential of bio-based coatings to meet both environmental and performance-driven demands across multiple sectors.

The global market for biodegradable plastic would be valued at USD 4.1 billion. During the projection period, it is expected to grow at a compound annual growth rate (CAGR) of 9.7%. The packaging industry is anticipated to expand by over 3% year between 2018 and 2028, reaching approximately $ 1.2 trillion (Four key trends such as Economic and demographic growth, Sustainability, Consumer Trends and Brand owner trends that will outline the forthcoming of packaging to 2028, 2021)[40]. Regulatory frameworks, such as the European Union’s Green Deal and carbon tax schemes, have incentivized the adoption of bio-based solutions, with companies launching bio-based resin coatings in 2023 to comply with stringent VOC standards[41]. The integration of agricultural and food waste, such as lignin and cellulose, into coating formulations further enhances sustainability by reducing costs and environmental footprints, aligning with circular economy objectives[42,43]. The Asia-Pacific region, particularly is emerging as a key growth market due to increasing demand for eco-friendly coatings in construction and packaging. Despite these advancements, several challenges hinder the widespread adoption of bio-based coatings. The higher cost of bio-based feedstocks compared to petrochemical alternatives, coupled with limited production capacity, poses significant barriers to scalability[44]. Achieving performance parity with fossil-based coatings, particularly in terms of durability and adhesion, remains a critical hurdle, necessitating further research and development. Supply chain constraints, including the regional availability of renewable feedstocks, increase transportation costs and carbon emissions, undermining sustainability goals. Additionally, the lack of standardized definitions and certifications for bio-based content complicates market acceptance and regulatory compliance[45,46]. Addressing these challenges requires concerted efforts in feedstock diversification, process optimization, and global harmonization of standards.

Looking ahead the future of bio-based coatings hinges on continued innovation and strategic collaboration. The exploration of novel feedstocks, such as secondary agricultural residues, promises to enhance supply chain stability and reduce costs. Advances in biotechnology and green chemistry are paving the way for non-isocyanate systems and Safe and Sustainable by Design (SSbD) frameworks, which prioritize environmental and health safety[47,48]. Collaborative initiatives to develop the bio-based solvent Cyrene, exemplify the potential of interdisciplinary efforts to scale sustainable solutions[49]. Furthermore, ongoing investment in chemical recycling and biomass balance processes will facilitate the integration of recycled and bio-based feedstocks, enhancing the circularity of coating production. These developments position bio-based coatings as a cornerstone of sustainable industrial practices in the coming decades.

2.1.1 Transition from Petroleum-Based to Bio-Based Resins

The transition from petroleum-based to bio-based resins represents a pivotal shift in materials science, driven by the urgent need to address environmental concerns, resource scarcity, and the demand for sustainable industrial practices. Petroleum-based resins, widely used in industries such as packaging, automotive, and construction, are derived from non-renewable fossil resources and contribute significantly to greenhouse gas emissions and environmental pollution due to their non-biodegradable nature[50]. In contrast, bio-based resins, synthesized from renewable resources such as plant oils, starches, or lignocellulosic biomass, offer a promising alternative by reducing carbon footprints and enhancing biodegradability. This section reviews key studies exploring this transition, focusing on the development, performance, and challenges of bio-based resins as viable substitutes for their petroleum-based counterparts.

Research on bio-based resins has gained momentum as advancements in biotechnology and green chemistry have enabled the synthesis of high-performance materials. For instance, studies have demonstrated that bio-based epoxy resins, derived from vegetable oils such as soybean or linseed, exhibit mechanical properties comparable to petroleum-based epoxies while offering improved environmental profiles. These resins were produced through epoxidation processes that functionalize plant-derived triglycerides, enabling their use in composites and coatings[51].

Similarly, bio-based polyesters, such as polylactic acid (PLA) derived from corn starch, have been extensively studied for their biodegradability and versatility in applications ranging from packaging to biomedical devices[52]. These studies highlight the potential of bio-based resins to meet industrial performance standards while aligning with sustainability goals.

Despite these advancements, the transition to bio-based resins faces significant challenges, as noted in the literature. One critical issue is the cost and scalability of production. Bio-based feedstocks, while renewable, often require complex processing and compete with agricultural resources, raising concerns about land use and food security[53,54]. Additionally, the mechanical and thermal properties of some bio-based resins, such as PLA, can be inferior to petroleum-based alternatives under certain conditions, limiting their application in high-performance context[52]. Research has also pointed the need for improved lifecycle assessments (LCAs) to quantify the environmental benefits of bio-based resins comprehensively as production processes can still generate significant energy demands[55]. These challenges underscore the importance of continued innovation in processing techniques and material formulations.

Recent studies have also explored hybrid approaches to bridge the gap between petroleum-based and bio-based resins. For example, incorporating bio-based fillers or additives into petroleum-based matrices can enhance sustainability without compromising performance. Such hybrid systems have shown promise in applications like automotive composites, where partial bio-based content reduces environmental impact while maintaining structural integrity. Furthermore, advancements in catalyst development and recycling technologies are facilitating the integration of bio-based resins into circular economy models, where end-of-life materials can be repurposed or biodegraded efficiently[56,57]. These findings suggest that a gradual transition, combining bio-based and petroleum-based systems, may be a pragmatic strategy for industries seeking to balance performance, cost and environmental impact.

Therefore, the transition from petroleum-based to bio-based resins is a multifaceted endeavour that requires balancing environmental benefits with technical and economic feasibility. Studies have demonstrated the potential of bio-based resins to replace their petroleum-based counterparts in various applications, driven by innovations in material synthesis and processing. However, challenges such as scalability, cost and performance limitations necessitate further research and development. By addressing these hurdles through hybrid systems, improved LCAs, and recycling technologies, the materials science community can pave the way for a more sustainable future in resin-based manufacturing.

2.1.2 Environmental and Health Limitations of VOC-based Coatings

Volatile Organic Compounds (VOCs) are integral to many traditional coating formulations, valued for their ability to enhance application properties, drying times, and finish quality. However, their widespread use raises significant environmental and health concerns due to their chemical volatility and reactivity. This section examines the multifaceted limitations of VOC-based coatings, focusing on their environmental impact, health risks, and the regulatory pressures driving the shift toward safer alternatives. By analysing these challenges through case studies and empirical evidence, this discussion underscores the urgency of addressing VOC-related issues in coating technologies.

2.1.2(a) Environmental Impacts of VOC Emissions

VOC-based coatings contribute substantially to environmental degradation, primarily through the emission of organic compounds into the atmosphere during application and curing processes. These compounds, released as solvents evaporate, participate in photochemical reactions with nitrogen oxides under sunlight, forming ground-level ozone and secondary organic aerosols (SOAs). Ozone, a key component of smog, adversely affects air quality, leading to ecosystem damage and reduced agricultural yields[58]. For instance, a study on atmospheric chemistry demonstrated that VOC emissions from architectural coatings in urban areas significantly exacerbate ozone levels, with California's South Coast Air Basin reporting exceedances of federal ozone standards partly attributable to coating-related emissions[59,60]. Furthermore, SOAs contribute to particulate matter (PM2.5), which poses long-term risks to both environmental and human health by altering climate patterns and reducing visibility[60].

The environmental footprint of VOC-based coatings extends beyond air pollution. Improper disposal of unused coatings or cleaning solvents can lead to soil and water contamination. A case study in the Netherlands highlighted the ecological consequences of VOC-containing waste from industrial painting operations, which leached into groundwater, affecting local aquatic ecosystem[61]. These findings emphasize the need for stringent waste management protocols and the development of low-VOC or VOC-free alternatives to mitigate such environmental risks.

2.1.2(b) Health Risks Associated with VOC Exposure

The health implications of VOC-based coatings are equally concerning, as exposure to these compounds can result in both acute and chronic effects. During application, painters and nearby individuals are exposed to VOC vapor's which can cause respiratory irritation, headaches, and dizziness[62]. Prolonged exposure, particularly in poorly ventilated environments may lead to more severe outcomes, including neurological damage and increased cancer risk[63]. A longitudinal study found that workers in the painting industry exhibited higher incidences of respiratory disorders and solvent-related neurological symptoms, correlating with frequent VOC exposure[64]. These health risks are not limited to occupational settings; consumers using VOC-based paints in residential environments also face potential hazards, particularly vulnerable populations such as children and the elderly[65]. Indoor air quality is a critical concern, as VOCs emitted from coatings can persist long after application, contributing to sick building syndrome. A case study in Sweden examined residential buildings painted with high-VOC coatings and found elevated levels of toluene and xylene in indoor air, correlating with occupant reports of eye irritation and fatigue[66]. These findings highlight the need for improved ventilation standards and the adoption of low-VOC formulations to safeguard public health.

2.1.2(c) Regulatory and Industry Responses

The environmental and health limitations of VOC-based coatings have prompted stringent regulatory measures worldwide. In the European Union, the Directive on the Limitation of Emissions of Volatile Organic Compounds (1999/13/EC) imposes strict limits on VOC content in coatings, pushing manufacturers toward water-based or high-solid alternatives[67]. Similarly, in the United States, the Environmental Protection Agency (EPA) has established National Volatile Organic Compound Emission Standards for Architectural Coatings, which have significantly reduced VOC levels in consumer products[8]. These regulations reflect a global trend toward minimizing VOC-related harm supported by industry innovations in bio-based and low-VOC coating technologies.

The environmental and health limitations of VOC-based coatings present significant challenges that necessitate a multifaceted response. Their contribution to air pollution, ecosystem degradation, and health risks underscores the urgency of transitioning to sustainable alternatives. Regulatory frameworks, supported by empirical evidence from case studies, have driven progress, but gaps in performance and adoption barriers persist. By prioritizing innovation and public awareness, the coating industry can mitigate the adverse impacts of VOCs, fostering a healthier and more sustainable future.

2.1.3 Advantages of Using Vegetable Oils as Resin Precursors

One of the primary advantages of vegetable oils is their environmental sustainability. As renewable resources derived from agricultural feedstocks, vegetable oils present a lower carbon footprint compared to petroleum-based counterparts. Their production involves photosynthesis-driven carbon sequestration, which mitigates greenhouse gas emissions during cultivation[68]. Additionally, vegetable oils are biodegradable, offering an end-of-life advantage for polymer products, as they can decompose naturally without contributing to long-term environmental pollution. For instance, soybean oil-based resins have been shown to exhibit biodegradability under composting conditions, making them suitable for applications where environmental impact is a concern[69]. This aligns with the principles of green chemistry, promoting the development of eco-friendly materials.

Beyond sustainability, the chemical versatility of vegetable oils enhances their appeal as resin precursors. The triglyceride structure, characterized by ester groups and carbon-carbon double bonds, allows for functionalization through processes such as epoxidation, acrylation, or maleinization. These modifications enable the synthesis of resins with diverse mechanical and thermal properties. For example, linseed oil, with its high degree of unsaturation, is particularly suited for producing highly cross-linked resins with enhanced mechanical strength[70]. Similarly, castor oil's unique ricinoleic acid content provides hydroxyl groups that facilitate the formation of polyurethanes, offering flexibility and toughness[71]. This adaptability allows vegetable oil-based resins to be tailored for applications ranging from coatings to composites.

Vegetable oil-based resins also demonstrate competitive performance in industrial applications. Their ability to form durable, flexible and chemically resistant polymers makes them viable alternatives to conventional resins. For instance, soybean oil-based resins have been successfully employed in coatings, exhibiting adhesion and corrosion resistance comparable to petroleum-based systems[72]. Additionally, linseed oil-based resins are widely used in alkyd paints due to their rapid drying and film-forming properties, attributed to auto-oxidative cross-linking[73]. The economic advantage of vegetable oils, often derived from abundant and cost-effective crops, further enhances their industrial viability, particularly in regions with established agricultural infrastructure.

Therefore, as industries increasingly prioritize sustainable materials, vegetable oil-based resins present a promising pathway for reducing environmental impact without compromising performance. Continued research into optimizing their synthesis and expanding their applications will further solidify their role in the future of polymer chemistry.

2.1.4 Natural Oils and Fats as sources for Functional Coatings.

Natural oils derived from plants and seeds, such as soybean, linseed, and castor oils, offer abundant and renewable feedstocks for coatings due to their composition of three fatty acids bonded to glycerol via ester linkages (Fig 6). These oils can be chemically modified to produce resins and binders with enhanced adhesion, durability, flexibility, and hydrophobicity, making them ideal for water-resistant and anti-corrosion applications[74-77].

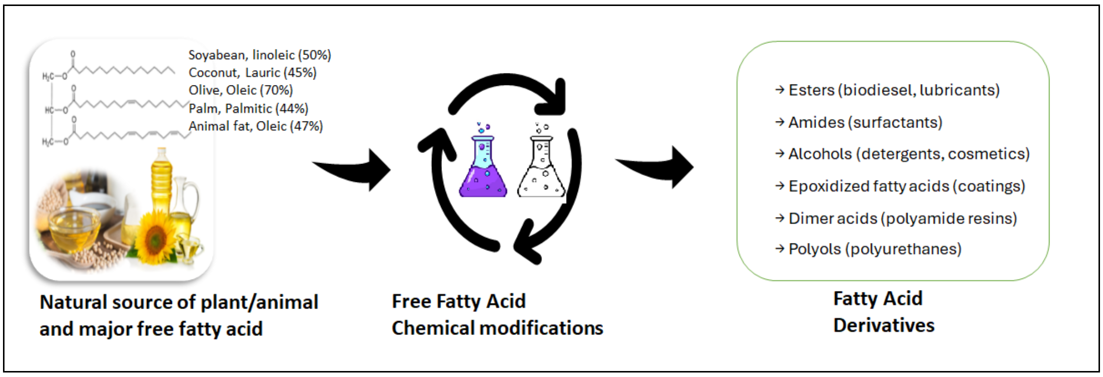

Figure 2.1 Typical Triglycerides Structure and Fatty Acid Derivatives

For instance, bio-based amino-oil coatings on seeds have been developed for controlled phosphate release, promoting eco-friendly agricultural practices.

Linseed oil has been utilized to modify polyurethane foams, advancing circular economy goals. Similarly, bio-based eugenol/clove oil has been polymerized via Mannich reactions to create solvent-free polyurethane coatings with superior physical, chemical, thermal, and mechanical properties[78]. Furthermore, soybean oil has been transformed into polyols through thiol-ene click reactions, with functionalization by silane, fluorine, and ethylene oxide units. These polymers outperform conventional polyurethanes in hardness, thermal stability, adhesion strength, and anti-corrosion properties[79]. Additionally, cashew nutshell liquid has been employed as a binder for polyurethane coatings, resulting in products with excellent scratch resistance, flexibility, solvent resistance, and corrosion resistance[80]. Linseed oil has also been modified through a one-step synthesis to produce multifunctional acrylate prepolymers for UV-cured coatings with high crosslinking density and strong adhesion, particularly to wood substrates[81]. Moreover, renewable coatings have shown promise in biomedical applications, as demonstrated by soybean oil-based coatings with crosslinked matrices and encapsulated biocides, which exhibit excellent biocompatibility and antibacterial properties[82].

Similarly, hybrid coatings based on canola oil, reinforced with silica nanoparticles, have addressed fastness challenges in bio-based materials through improved mechanical and thermal properties[83]. Furthermore, hybrid coatings from modified acetoacetylated soybean oil by adopting solvent-free, thiol- ene and transesterification approach using catalyst free and stimulated by UV-light. The novel functional and organic-inorganic coatings prepared by varying the concentration of amino-silicones compound which confirmed using FT-IR, NMR, and good viscoelastic analysis. The coatings product found to be promising due to good chemical and dynamic mechanical properties due to silicon cross linked in the structure[84]. Recent advancements in renewable coatings highlight the development of Real Michael-Addition (RMA) paints containing up to 53% renewable content, with future projections reaching 80%. These paints utilize polymeric resins synthesized from novel malonate-functional polyesters, acryloyl-functional oligomers, diethyl malonate, isorbide, and vegetable oils through base-catalysed Michael addition reactions.

The isorbide-based resins demonstrate excellent moisture resistance and improved adhesion on epoxy-amine primers, while vegetable oil-based coatings show superior surface appearance due to enhanced levelling characteristics[85]. Furthermore, functional coatings with both antimicrobial and anticorrosion properties have been developed using algae fatty acids and silver-doped eggshell hydroxyapatite on mild steel. These nanocomposite coatings exhibit excellent thermal properties, contact angle, flexibility, pencil hardness, and adhesion, making them promising for dual-purpose applications[86]. To address bacterial contamination on catheters, hybrid coatings were created from cashew linseed oil through epoxidation and acrylation, followed by chelation with metal ions. These coatings, formed at room temperature without initiators, demonstrated strong metal-ligand bonding confirmed by NMR and FT-IR spectroscopy. The resulting thin films exhibit remarkable antibacterial properties, thermal stability, and dynamic mechanical performance, making them suitable as non-leachable coatings to combat bacterial threats[87].

Similarly, green composites derived from methacrylated epoxidized sucrose soyate and reinforced with glass fibres surpass conventional vinyl ester composites in tensile strength, modulus, impact resistance, flexural strength, and thermal properties. These attributes position them as viable alternatives to petroleum-based resins in construction applications for both high and low-temperature uses[88]. Finally, a one-step process converted soybean oil into (acryloyl amino) ethyl soyate via direct esterification with N-(hydroxyethyl) acrylamide. The resulting products, copolymerized with styrene, methyl methacrylate, and vinyl acetate, have shown potential as sustainable replacements for petroleum-based resins in polymer production, latexes, adhesives, and dispersants[89].

Vegetable oil-based coatings have gained considerable attention in recent years due to their sustainability, biodegradability, and the potential to be modified for specific functional properties, such as insect repellent and flame retardancy. Flame retardant coatings are essential in various applications where reducing flammability is critical, including in construction, textiles, and electronics while those with insect repellent can be used to protect wooden houses in termite infested environment. Incorporating flame retardant properties into vegetable oil-based coatings combines environmental benefits with enhanced safety, making these coatings highly valuable. Therefore, some relevant research based on flame retardant compounds e.g. phosphate-based and insecticidal activities conducted will be mentioned in the subsequent paragraph.

A research work of Mustata et al.[90] on developing ecofriendly epoxy resin for wood protection against fungal attack using epoxide soya bean oil (ESO) and castor oil maleic anhydride (COMA) and methyl nadic (MN) as crosslinking agent. The coatings assessment revealed good thermal stability, and enhanced protection of the from fungal destruction which improved the durability of the wooden materials [90]. Yang et al. [91] focused on development of UV-curable coating derived from AESO modified with silicon to improved thermal stability, flame retardant properties with outstanding optical and electronic applications. This finding suggested using silicon modification to enhance thermal behaviors without compromising optical clarity in advance material applications [91].

Chang et al. [92] examined the integration of phosphoric acid into the polycarbonate oil (PCO) backbone, identifying 15 wt.% as the maximum incorporation level. The degree of phosphorylation was measured using proton nuclear magnetic resonance (^{1}H NMR) and confirmed by inductively coupled plasma optical emission spectroscopy (ICP-OES), with both methods providing consistent results. The study demonstrated a clear relationship between phosphoric acid content and phosphorylation, with structural changes analyzed via NMR and Fourier-transform infrared spectroscopy (FTIR). This research advances the understanding of bio-based epoxy blends and their thermal properties [92].

Sykam et al. [93] investigated the synthesis and characterization of multifunctional flame retardants (HTP-FRs) grafted onto bio-polyol-based polyurethanes (PUs) via azide-alkyne click chemistry. Structural analysis was conducted using ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, while molecular weights were measured with electrospray ionization mass spectrometry (ESI-MS). Thermogravimetric analysis (TGA) confirmed enhanced thermal stability of the synthesized PUs. The synergy of 1,2,3-triazole and phosphate groups in HTP-FRs suggests potential industrial applications in flame retardancy and corrosion protection [93].

A study conducted and reported by Yin et al. [94] on the synthesis of a soy-castor oil-based polyurethane acrylate prepolymer (SCPUA) using epoxidized soybean oil and ricinoleic acid. The addition of a halogen-free flame retardant, PSMAM, enhances the flame retardancy, thermal stability, and mechanical properties of the coatings. UV-curable coatings are highlighted for their efficiency, environmental friendliness, and low energy consumption [94]. Similarly, Moreno et al. [95] developed a flame-retardant thermosetting resin from high oleic sunflower oil using aza- and phospha-Michael additions. Key materials include high oleic sunflower oil, methyl oleate, and 1,3-bis(phenylphosphino)propane dioxide. The study found that introducing phosphorus significantly improved the flame-retardant properties, with limiting oxygen index values increasing from 21.5 to 38.0 [95].