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Review

Chemical Functionalization of Camelina, Hemp, and Rapeseed Oils for Sustainable Resin Applications: Strategies for Tailoring Structure and Performance

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Abstract

This review examines the chemical functionalization of Camelina, hemp, and rapeseed oils for the development of sustainable bio-based resins. Key strategies, including epoxidation, acrylation, and click chemistry, are discussed in the context of tailoring molecular structure to enhance reactivity, compatibility, and material performance. Particular emphasis is placed on overcoming the inherent limitations of vegetable oil structures to enable their integration into high-performance polymer systems. The agricultural sustainability and environmental advantages of these feedstocks are also highlighted alongside the technical challenges associated with their chemical modification. Functionalized oils derived from Camelina, hemp, and rapeseed have been successfully applied in various resin systems, including protective coatings, pressure-sensitive adhesives, UV-curable oligomers, and polyurethane foams. These advances demonstrate their growing potential as renewable alternatives to petroleum-based polymers and underline the critical role of structure–property relationships in designing next-generation sustainable materials. Ultimately, the objective of this review is to distill the most effective functionalization pathways and design principles, thereby illustrating how Camelina, hemp, and rapeseed oils could serve as viable substitutes for petrochemical resins in future industrial applications.

Keywords: chemical modification; acrylated vegetable oils; bio-based polyurethanes; structural coatings; epoxidized plant oils

Academic Editor: Victoria V. Volkis

Received: 26 April 2025
Revised: 23 June 2025
Accepted: 3 July 2025
Published: 10 July 2025

Citation: Nadim, E.; Paraskar, P.; Murphy, E.J.; Hesabi, M.; Major, I. Chemical Functionalization of Camelina, Hemp, and Rapeseed Oils for Sustainable Resin Applications: Strategies for Tailoring Structure and Performance. *Compounds* **2025**, *5*, 26. https://doi.org/10.3390/compounds5030026

1. Introduction

The escalating demand for environmentally sustainable materials has catalyzed extensive research into bio-based resins, coatings, and adhesives as promising substitutes for conventional petroleum-derived polymers [1]. Plant seed oils have emerged as promising raw materials for thermosetting resins, exemplifying the broader transition toward bio-based alternatives. However, in their native state, these oils exhibit limited reactivity for direct industrial application, thereby necessitating sophisticated chemical functionalization to introduce crosslinkable groups [1].

A prominent strategy for enhancing the reactivity of vegetable oils involves epoxidation, yielding epoxidized vegetable oils that are widely utilized as secondary plasticizers in polyvinyl chloride formulations and as renewable precursors to epoxy resins [2]. The introduction of reactive oxirane groups enables further chemical transformations, including conversion into polyols for polyurethane synthesis or modification into maleinized and

acrylated derivatives [2]. In many cases, complete curing still needs rigid comonomers or extra hardeners (e.g., polyamines and anhydrides) because of limited oxirane content [2].

Beyond epoxidized derivatives, bio-based alkyd and polyurethane resins derived from vegetable oils are being developed as drop-in replacements for petroleum-based resins [3]. Nevertheless, challenges remain, including inconsistent reactivity profiles, phase separation in hybrid formulations, and continued reliance on petrochemical-based isocyanates [3]. Variations in fatty acid unsaturation and hydroxyl functionality dictate formulation routes and ultimately control the mechanical and thermal properties of the resulting resins.

This review focuses on the chemical functionalization of three non-food vegetable oils—Camelina (Camelina sativa), hemp (Cannabis sativa), and rapeseed (Brassica napus)—selected for their adaptability to regional agricultural conditions, sustainability credentials, non-food applicability, and favorable chemical characteristics for advanced polymer synthesis [4–6] due to their high unsaturation. Vegetable oils can be categorized as drying, semi-drying, or non-drying, based on the degree of unsaturation within their triglyceride structures. Those enriched with fatty acids containing more than two double bonds exhibit drying behavior, whereas oils dominated by di-unsaturated fatty acids are considered semi-drying. In contrast, oils primarily composed of mono-unsaturated fatty acids are classified as non-drying [7]. Camelina and hemp oils, characterized by elevated proportions of tri-unsaturated linolenic and linoleic acids, are categorized within the semi-drying to drying classes, while rapeseed oil is classified as semi-drying (Table 1). The notably high iodine values of these oils—Camelina oil (143–154 g I_2/100 g) [8], rapeseed oil (94–100 g I_2/100 g) [9], and hemp oil (up to 170 g I_2/100 g) [10]—reflect their increased density of reactive carbon–carbon double bonds, thereby providing enhanced theoretical epoxide or acrylate functionalities [11].

Table 1. Fatty acid composition of Camelina, hemp, and rapeseed oils.

Fatty Acid (%) (CN [a]:DB [b])	Camelina [12]	Hemp [13]	Rapeseed [14]
Palmitic (16:0)	5.3–6.8	7.3–7.7	3.4–5.1
Palmitoleic (16:1)	n.d. [c]	0.1–0.2	0.2–0.3
Stearic (18:0)	2.5–2.7	2.4–2.6	2.5–2.6
Oleic (18:1)	12.6–18.6	12.8–13.3	64.7–66.0
Linoleic (18:2)	14.3–19.6	56.7–57.7	16.3–16.3
α-Linolenic (18:3)	32.6–38.4	17.8–18.7	7.5–7.6
γ-Linolenic (18:3)	n.d.	3.2–3.6	n.d.
Arachidic (20:0)	1.2–1.4	n.d.	0.9–1.01
Gondoinic (20:1)	12.4–16.8	0.7–0.81	n.d.
Eicosadienoic (20:2)	1.3–2.0	n.d.	n.d.
Eicosatrienoic (20: 3)	0.8–1.7	n.d.	n.d.
Behenic (22:0)	0.2–0.3	0.1–0.2	n.d.
Erucic (22:1)	2.3–2.9	n.d.	1.0–2.0

[a] CN: Carbon Number; [b] DB: Number of Double Bonds; [c] n.d.: Not Determined.

Camelina is particularly valued for its resilience to environmental stresses, short cultivation cycle, and capacity to grow on marginal lands [10,12]. Hemp distinguishes itself through its ability to thrive in contaminated soils with minimal agrochemical input, while simultaneously contributing to soil remediation and improvement [11,13] (see Section 1.1). Rapeseed is extensively cultivated across Europe for both food and industrial purposes. While Canadian breeding programs successfully eliminated erucic acid to produce low-erucic canola varieties for edible oil, traditional high-erucic cultivars continue to be grown for non-food applications [9,14–16]. The resulting erucic-rich oils represent valuable bio-based feedstocks that do not compete with the edible oil supply chain. Consequently, these oils facilitate the formation of densely crosslinked polymeric networks, significantly enhancing the resultant thermomechanical properties of bio-derived resins [17–19].

The fatty acid compositions of Camelina, hemp, and rapeseed oils are presented in Table 1. By reviewing recent advancements in chemical modification strategies and evaluating the corresponding performance metrics of these bio-based resins, this article aims to provide a comprehensive understanding of both the potential and the persistent challenges associated with their industrial application. An overview of the potential applications of these oils as renewable substitutes for petroleum-based chemicals is presented in Figure 1. The following sections examine the underlying chemical frameworks and explore formulation strategies designed to tailor molecular structure and optimize performance in advanced polymer systems.

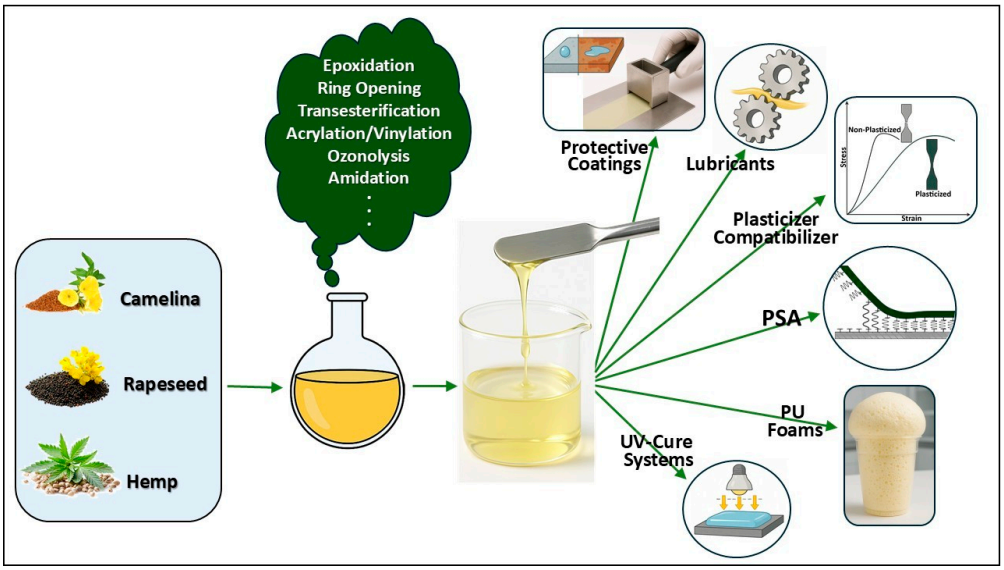


Figure 1. Industrial potential of Camelina, rapeseed, and hemp oils.

Earlier reviews surveyed plant oil modification and focused on high-volume feedstocks such as soybean, linseed, palm, or castor, but none focused on Camelina, hemp, and rapeseed, the three regionally adaptive, non-food oils most relevant to Europe's resin sector. Here we compare their composition-dependent reactivity across established routes (epoxidation, hydroformylation, acrylation, and click chemistry) and introduce emerging intensification methods such as deep-eutectic-solvent epoxidation, microwave, and continuous-flow processing, while outlining the persisting hurdles, composition variability, catalyst recyclability, and cost-effective scale-up that still delay full industrial adoption.

1.1. Agricultural Benefits of Camelina, Hemp, and Rapeseed

Beyond molecular tunability, the selection of feedstocks must also consider the reliability and responsibility with which a crop can be cultivated. Camelina, hemp, and rapeseed

exhibit exceptional regional adaptability, perform well with minimal agrochemical input, and integrate efficiently into existing crop rotations (Table 2)—traits that underpin a stable, low-carbon supply chain. These agronomic strengths are therefore as critical as the functionalization chemistry itself and are outlined in the following.

Table 2. Comparison of yield, oil content, and key sustainability metrics for Camelina, hemp, and rapeseed.

Seed	Yield (t ha^{-1}) [6,16]	Oil Content (Wt%) [4,20–22]	Sustainability Metrics
Camelina	1.27–3.3	30–45	Low water and nutrient input Short season (85–100 days) Tolerates salinity, frost, and marginal soils
Rapeseed	2.5–3.5	40–48	Fast biomass gain High carbon-sequestration potential Phytoremediates heavy metals and radionuclides Adaptable to diverse European soils
Hemp	1–1.5	26–42	Improves soil structure and nutrient cycling Low pesticide requirement Weed suppression

t ha^{-1}: Tones/hectare.

1.1.1. Camelina

Camelina (Camelina sativa), commonly known as false flax, is an oilseed crop indigenous to Europe and southeastern Asia. Historically, it served as an important edible oil source before being displaced by higher-yielding alternatives such as canola and wheat [12,23–25]. Renewed interest in Camelina is largely driven by its favorable agronomic traits, including shallow rooting depth, low water requirements, a short growing season (85–100 days), and exceptional winter hardiness. These attributes enable double cropping and allow cultivation on saline, frosty, or otherwise marginal soils. Economically, Camelina oil offers a sustainable alternative to castor oil, particularly in view of castor's geographic limitations and price volatility [26].

1.1.2. Hemp

Recent years have seen a resurgence of interest in hemp (Cannabis sativa) owing to its versatile applications and agronomic advantages. Hemp seed oil is valued for its beneficial nutritional profile, particularly its high content of essential fatty acids associated with therapeutic effects such as cholesterol reduction, alleviation of dermatitis, and mitigation of hypertension. However, the high degree of unsaturation inherent in hemp seed oil substantially increases its susceptibility to oxidative degradation, limiting its direct application in food products [27]. Agriculturally, hemp exhibits a rapid growth cycle—reaching heights of up to 5 m within three to four months—and demonstrates an exceptional carbon sequestration capacity, absorbing CO_2 at rates exceeding those of comparable forested areas. It also displays remarkable environmental adaptability, tolerating diverse soil conditions and contributing to phytoremediation by extracting heavy metals, organic pollutants, and radionuclides from contaminated soils [23]. These combined traits enhance its potential as a sustainable industrial crop. Industrial hemp seeds yield between 26% and 42% oil, while the associated lignocellulosic biomass presents opportunities for low-carbon biofuel production, including bioethanol, biobutanol, and biodiesel, via microbial fermentation [28,29].

1.1.3. Rapeseed

Rapeseed (Brassica napus) is widely recognized in Europe as a high-performing break crop within winter cereal rotations. Its inclusion improves soil structure and enhances nitrogen use efficiency, collectively supporting nutrient cycling and farm profitability. Competitive yields and favorable gross margins relative to other broadleaf crops have reinforced rapeseed's role as a major cash crop across Germany, France, Poland, and the United Kingdom, even as pest pressures and regulatory landscapes evolve [30]. Rapeseed's high oil productivity—approximately 3.5 tons per hectare for winter cultivars and 2.5 tons per hectare for spring varieties—has driven its widespread adoption [31]. Beyond its agronomic value, rapeseed oil aligns with renewable agricultural practices, serving not only as a feedstock for biodiesel but also as a precursor for environmentally responsible materials that offer sustainable alternatives to petroleum-derived products [32].

2. Functionalization Strategies of Camelina, Hemp, and Rapeseed Oils for Bio-Based Resin Development

Functionalization strategies constitute the scientific basis for transforming native vegetable oils into reactive, structurally tunable, and industrially applicable building blocks. In the context of bio-based resin development, these chemical modifications are not merely preparatory but central to defining the intrinsic reactivity, interfacial compatibility, and network-forming potential of oils such as those of Camelina, hemp, and rapeseed.

As discussed, native vegetable oils lack sufficient reactive functional groups required for direct use in advanced polymer formulations. Chemical modification through various functionalization strategies introduces hydroxyl, epoxy, or carboxyl groups to enhance reactivity, crosslinking capability, and integration into high-performance resin systems, thus enabling their transformation into diverse polymer types. The choice of functionalization approach significantly influences the mechanical properties, viscosity, and adhesion characteristics of the resulting coatings and adhesives [33,34].

Several chemical strategies have been explored to improve the reactivity of vegetable oils, with epoxidation, transesterification, hydroformylation, thiol-ene reactions, and ozonolysis among the most widely employed techniques [33,35,36]. Each method modifies the triglyceride structure differently, tailoring the molecular architecture to suit specific polymerization and application requirements, as explored in subsequent sections. Hydroformylation, for example, introduces aldehyde and hydroxyl functionalities, substantially increasing the oil's reactivity toward isocyanates; however, the reliance on costly metal catalysts such as rhodium and nickel remains a major barrier to industrial scalability [37]. Thiol-ene reactions offer an alternative route to synthesizing polyols with high hydroxyl values under relatively mild conditions, although concerns regarding reaction scalability and efficiency persist [33]. Ozonolysis, primarily applied to unsaturated vegetable oils, enables the production of polyols with controlled molecular weight distribution and enhanced mechanical properties; however, acid formation during the process may compromise the final network integrity if not properly managed [33].

In practical applications, combinations of these functionalization methods are often employed to leverage the advantages of each individual technique while mitigating their respective limitations. These strategies serve as a conceptual framework for understanding the transformation of Camelina, hemp, and rapeseed oils into high-value polymeric materials. In the following sections, these core strategies are examined in detail through their implementation in specific polymer classes—such as polyamides, alkyds, polyurethanes, and acrylates—highlighting their structural consequences, performance outcomes, and industrial potential.

3. Application-Oriented Polymerization Pathways Using Modified Camelina, Hemp, and Rapeseed Oils

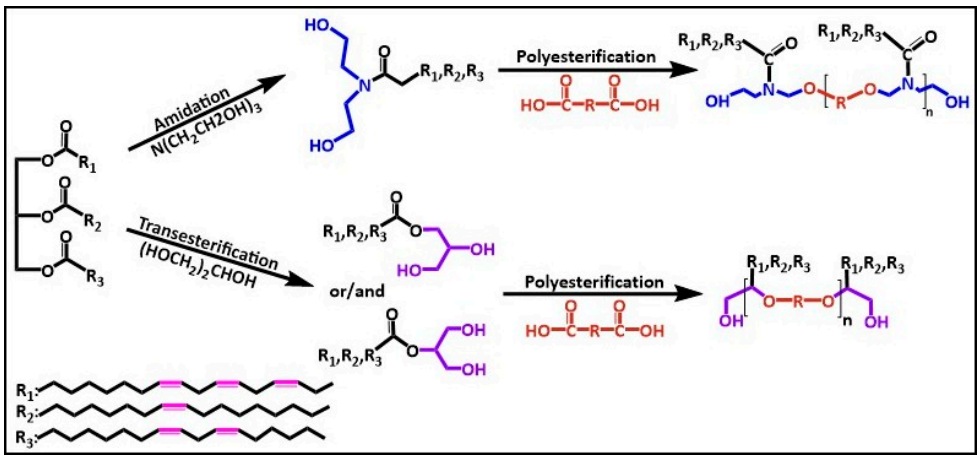
While the chemical modification pathways common to triglyceride-based oils, such as epoxidation, acrylation, and transesterification, are broadly similar, the resulting product composition, reactivity, and polymer performance are strongly dictated by the unique fatty acid profile of each oil. Accordingly, this section outlines general polymerization strategies while highlighting specific applications and outcomes for Camelina, hemp, and rapeseed oils.

3.1. Polyamides

Polyamide resins derived from vegetable oils are typically synthesized through reactions involving dimer acids, which are predominantly formed via the dimerization of C18 unsaturated fatty acids, such as oleic and linoleic acids. These dimer acids offer several advantageous properties, including environmental compatibility, chemical reactivity, biodegradability, low toxicity, and a liquid state at room temperature, which enhances their solubility in hydrocarbon solvents. Due to their relatively high molecular weight compared to traditional diacids, polyamides synthesized from dimer acids exhibit enhanced flexibility, improved solubility in alcohols, and superior compatibility with various resins and additives. Bio-based polyamide resins are widely utilized as binders in industrial applications, including paints, inks, varnishes, and heat-seal coatings. Furthermore, they serve as essential components of thixotropic agents, which regulate viscosity under shear conditions and facilitate consistent, controlled rheological behavior within coating systems [38].

3.2. Polyesterification

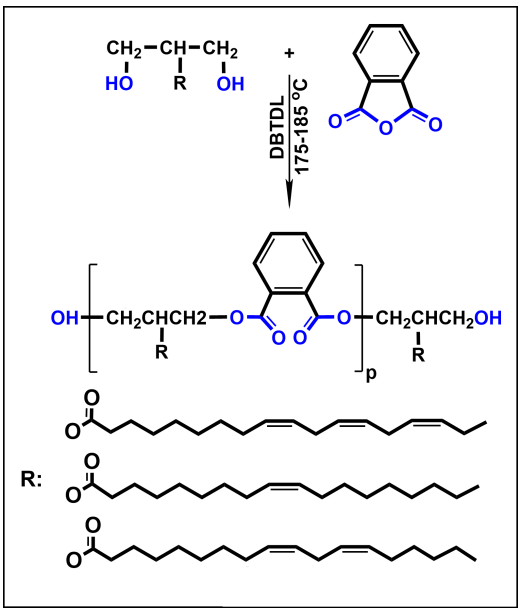
Polyester synthesis from plant oils typically involves polycondensation reactions between bifunctional carboxylic acids and glycols derived from triglycerides (Scheme 1). In practice, polyesterification is often combined with additional chemical modifications, such as amidation to form polyesteramides, or with polyols and dicarboxylic acids to produce alkyd resins [39,40]. Alkyd resins and polyesteramides represent two primary classes of modified vegetable oil-based polyesters. Alkyd resins are synthesized by reacting vegetable oils with polyols and dicarboxylic acids, whereas polyesteramides are produced through combined amidation and esterification reactions. Both pathways significantly enhance the functional properties of vegetable oils, expanding their range of industrial applications.



Scheme 1. Schematic representation of amidation/transesterification of triglycerides followed by polyesterification reactions.

3.2.1. Alkyd Resins

Alkyd resins are among the earliest commercially viable bio-based polymers derived from triglyceride oils. They are typically synthesized via either the monoglyceride method or the fatty acid method. In the monoglyceride route, triglyceride oils—such as rapeseed oil [41]—undergo alcoholysis, a transesterification reaction with a stoichiometric amount of a polyol, typically glycerol, to form monoglyceride intermediates. In the subsequent polyesterification stage, the hydroxyl groups generated during alcoholysis react with polybasic acids or their anhydrides (e.g., glutaric, maleic, phthalic, and succinic acids) to construct the polyester backbone of the alkyd resin (Scheme 2) [39,42].



Scheme 2. Synthesis of an alkyd resin from phthalic anhydride and monoglyceride (adapted from [36], open access).

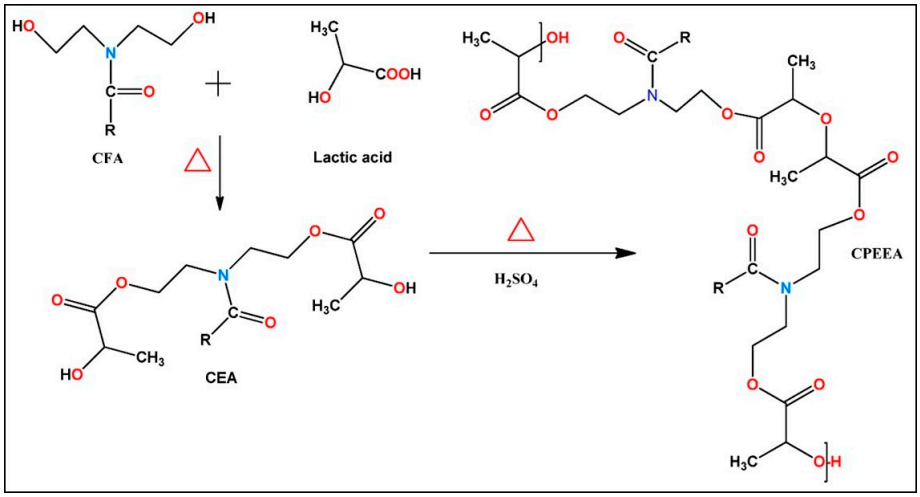
Rapeseed oil has been employed as a lipid source for alkyd resins formulated for printing inks, where the selection of difunctional monomers significantly influences processing parameters such as viscosity and flow behavior, as well as final coating properties, including film formation, hardness, and durability [42]. Nimbalkar et al. [43] developed a water-reducible alkyd resin from canola (rapeseed) oil via polycondensation with glycerol and anhydrides, followed by grafting with styrene and acrylamido tertiary butane sulfonic acid. Coatings based on this system exhibited significant improvements in hardness, scratch resistance, adhesion, thermal stability, and chemical and solvent resistance.

An additional sustainable approach involves enzyme-catalyzed glycerolysis, demonstrated using Camelina oil to produce monoglycerides, which were subsequently esterified with dibasic acids to yield alkyd diols. These diols were then utilized to synthesize polyurethane coatings with excellent thermal, mechanical, and chemical properties, along with outstanding adhesion, toughness, and corrosion resistance, making them suitable for outdoor applications [39]. Nosal and colleagues further synthesized alkyd resins from Camelina oil through alcoholysis with glycerol or other polyols in the presence of lithium hydroxide as a catalyst, followed by polyesterification with phthalic and maleic anhydrides at elevated temperatures [44].

3.2.2. Polyesteramides

Alternating polyesteramides are copolymers that integrate the advantageous properties of both polyamides and polyesters. When synthesized from triglyceride oils, these

oil-modified polyesteramide resins form an advanced class of amide-functionalized alkyds, often exhibiting superior performance compared to conventional alkyd resins. A common method to further enhance polyesteramide properties is their reaction with isocyanates, introducing urethane linkages into the polymer network [42]. This modification improves mechanical strength, chemical resistance, and thermal stability [45]. For instance, polyols based on canola oil were synthesized via a combination of amidation and polyesterification reactions (Scheme 3) and subsequently used in the preparation of urethane-based coatings exhibiting superior anticorrosive properties [46].

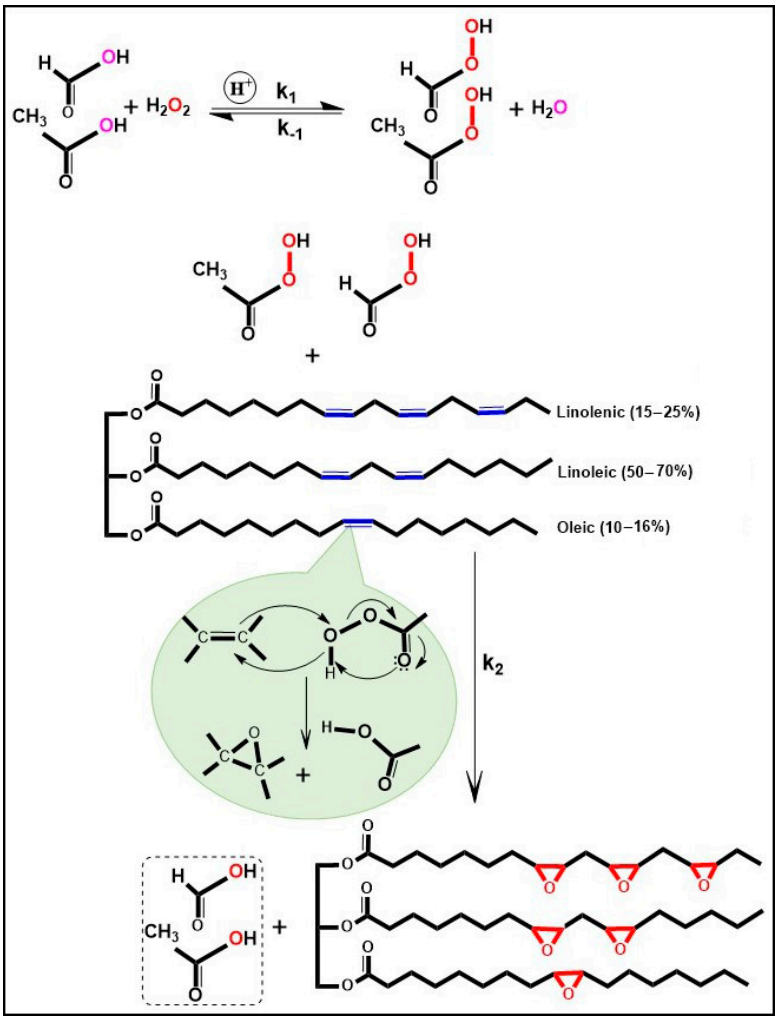


Scheme 3. Synthetic pathway for canola (rapeseed) oil-based poly(ester-ether) amide (adapted from [46], open access). Abbreviations: CEA, canola oil esteramide; CPEEA, canola oil polyesteramide.

Another notable example includes polyesteramide polyols derived from Camelina oil, synthesized via transamidation of triglycerides with diethanolamine, followed by reaction with citric, itaconic, or phthalic acids. The resulting polyols demonstrated satisfactory thermal stability, biocarbon contents of up to 61.6%, and suitability for polyurethane coatings intended for indoor, non-wet applications [45].

3.3. Epoxidation

Another widely employed functionalization route for unsaturated plant oils involves converting the carbon–carbon double bonds into reactive epoxy groups, yielding epoxidized intermediates that serve as versatile building blocks for a broad range of bio-based polymers. A widely employed functionalization route for unsaturated plant oils is the catalytic epoxidation of their carbon–carbon double bonds, a process that yields reactive epoxy intermediates while suppressing side reactions such as premature ring opening. Multiple strategies have been employed to improve epoxidation efficiency: metal-catalyzed methods enhance both selectivity and yield, while chemoenzymatic approaches provide more sustainable alternatives. Nevertheless, the classical Prilezhaev route, an in-situ peracid epoxidation with performic or peracetic acid, remains the most widely applied technique. It is commonly catalyzed by strong mineral acids such as sulfuric, phosphoric, nitric, or hydrochloric acid, while heterogeneous catalysts, including acidic ion-exchange resins, sulphonated alumina, and zeolites, have also been explored to improve yield efficiency (Scheme 4) [10,47,48].



Scheme 4. Schematic representation of hemp oil epoxidation using in situ-generated peracids in the presence of an ion-exchange resin (adapted from [10], open access).

The resulting epoxidized oils can be directly formulated into thermosetting epoxy resins, typically cured with anhydrides, for applications such as coatings and adhesives. Alternatively, epoxidized oils may undergo ring-opening reactions with nucleophilic agents—including water, alcohols, halogens, amines, or lactic acid—to introduce new functionalities. Additional post-epoxidation modifications, such as acrylation, hydrogenation, and carbonation, further expand their utility by introducing new reactive sites. These modifications allow the production of plant-based compounds tailored for applications ranging from flexible elastomers to rigid thermosets.

Despite these advances, direct polymerization of epoxidized vegetable oils often results in mechanical properties inferior to those of petroleum-derived systems. This is primarily attributed to the limited reactivity of epoxy groups, intramolecular interactions that inhibit effective crosslinking, and a tendency toward side reactions. Nevertheless, epoxidized vegetable oils remain promising renewable feedstocks for the development of sustainable polymeric materials [42,49].

In addition to resin applications, the incorporation of epoxidized vegetable oils into alkyd resins enhances crosslink density, reduces drying times, and improves hardness and thermo-oxidative stability [37]. Epoxidized plant oils have also demonstrated strong potential as biolubricants, offering reduced friction and wear, improved thermal stability, and strong metal surface adhesion [50]. Furthermore, epoxidized derivatives serve as

plasticizers and compatibilizers in thermoplastic starch–polylactic acid blends, facilitating enhanced material compatibility and mechanical performance [51].

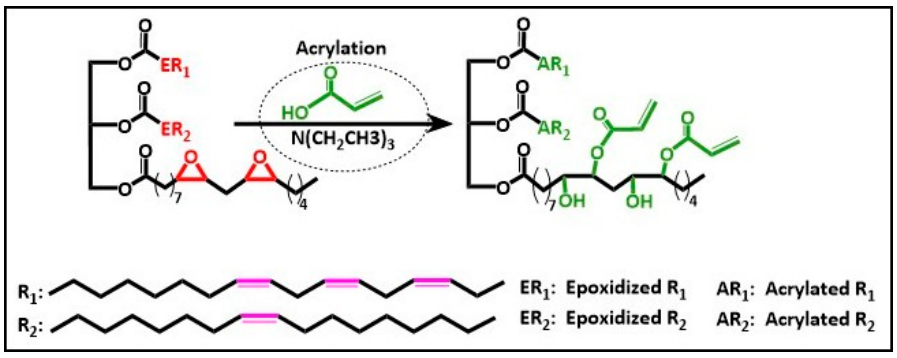
Specifically, epoxidized triglycerides derived from Camelina oil have been successfully employed as monomers and polymer building blocks for polyurethane coatings [52–55]. Similarly, epoxidized rapeseed oil has been incorporated into biopolymer blends, adhesives, and coatings, improving polymer network formation, cohesive bonding, and mechanical durability [56]. Valorization of hemp oil through epoxidation strategies has also been demonstrated. For example, Shuttleworth et al. reported the epoxidation of hemp oil using in situ-generated peroxyacetic acid, followed by crosslinking catalyzed by 4-dimethylaminopyridine, yielding flexible and transparent films. Incorporation of halloysite nanotubes further enhanced water resistance and mechanical integrity [27]. Omonov et al. formulated hemp-based epoxy adhesives using citric acid and trimellitic anhydride as curing agents for biocomposite applications [57].

Additional strategies involve the use of maleinized hemp seed oil as a bio-based curing agent for epoxidized soybean oil. The resulting coatings demonstrated strong adhesion, self-healing functionality, and high resistance to corrosive environments [58]. Gupta et al. further reported the antifriction and tribological performance of epoxidized rapeseed oil, which exhibited a significant reduction in the coefficient of friction under metal-to-metal contact conditions [59].

3.4. Acrylation and Vinylation

Acrylation and vinylation represent key post-epoxidation modification strategies that significantly expand the chemical functionality and application potential of vegetable oils. Early approaches involved copolymerization with vinyl monomers such as cyclopentadiene, α-methylstyrene, or styrene, leading to improved film-forming properties and broader use in surface coatings [42]. Although vinyl-modified triglyceride oils are predominantly employed in the paint industry, their favorable light color, transparency, toughness, rigidity, and thermal stability suggest broader potential for advanced material formulations [42].

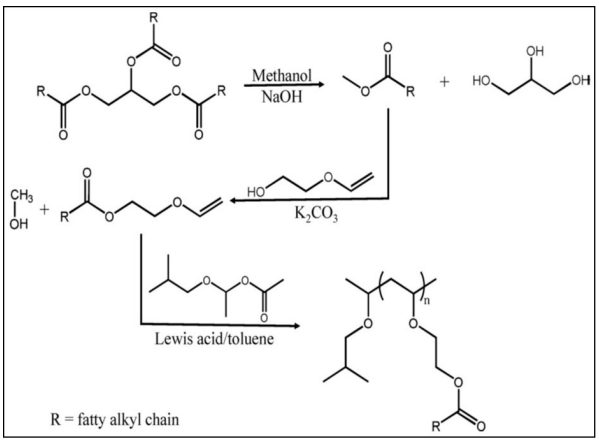
In acrylation, the strained oxirane rings of epoxidized vegetable oils are opened with acrylic acid in the presence of catalysts (e.g., triethylamine and triphenylphosphine oxide) and inhibitors that suppress unwanted free radical reactions. This transformation yields acrylated epoxidized plant oils, which serve as polymerizable monomers (Scheme 5) [60].



Scheme 5. Schematic representation of acrylation of epoxidized plant oils (adapted from [60], open access).

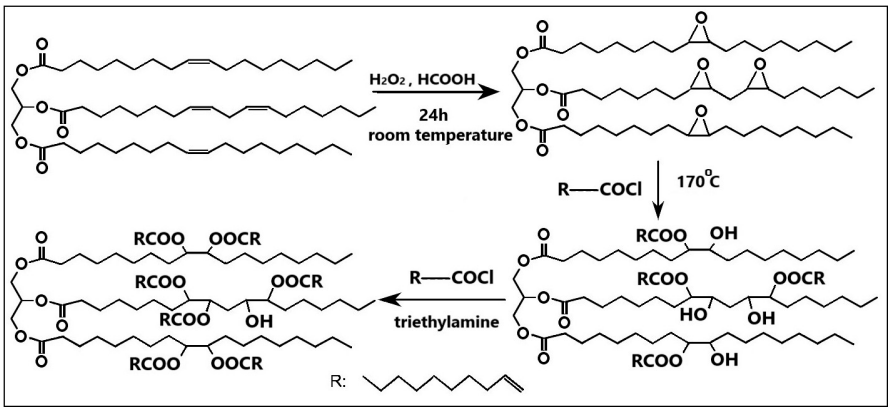
Acrylated epoxidized triglycerides have been applied in UV-curable coatings, biodegradable foams, bioplasticizers, and composites for coating plastics, paper, and wood. However, limitations such as variability in oil quality, side reactions during modification, and lower yields compared to petrochemical feedstocks still constrain large-scale deployment.

Camelina oil has emerged as a versatile platform for the synthesis of UV-curable acrylates and vinyl derivatives. Sung et al. prepared bio-based acrylates by reacting Camelina oil fatty acids with cardanyl glyceride ether, yielding UV-curable wood coatings with excellent thermal stability, hardness, tensile strength, and solvent resistance [61]. Kalita et al. synthesized plant-based polyvinyl ether monomers from Camelina oil, polymerized via cationic polymerization (Scheme 6), enabling ambient-cured thermoset coatings with low energy demands and reduced material waste [62].



Scheme 6. Synthesis of plant-based polyvinyl ether monomer followed by cationic polymerization, Reprinted from [62] with permission; Copyright Elsevier 2018.

Further studies developed multifunctional photopolymerizable vinyl oligomers from rapeseed oil through multistep epoxidation, ring opening, and esterification processes (Scheme 7), producing UV-cured materials with strong mechanical and thermal performance [63].



Scheme 7. Reaction pathway for the production of multifunctional vinylic oligomers based on rapeseed oil (adapted from [63], open access).

Additional examples include the preparation of acrylated intermediates from methyl esters of Camelina fatty acids for latex coatings [53], photocurable hydrophilic monomers derived from epoxidized Camelina oil [64], and interpenetrating polymer networks based on Camelina oil and dimethacrylated ethylene glycol [65]. UV-cured pressure-sensitive adhesives formulated from dihydroxyl acrylated derivatives of epoxidized Camelina oil have also shown excellent cohesive strength and balanced peel–tack properties [25,61].

Rapeseed oil has been extensively modified via sequential epoxidation, acrylation, and methacrylation, yielding coatings with high biocarbon contents, enhanced flexibility, hydrophobicity, and strong mechanical properties [61,66–68]. Hemp oil has also been

successfully functionalized via acylation of epoxidized intermediates, producing resins with promising mechanical performance in fiber-reinforced composites [69,70]. Despite ongoing progress, challenges such as high viscosity, incomplete epoxide homopolymerization, autocatalytic curing tendencies, and vitrification-related diffusion limitations still need to be addressed to fully optimize the performance and scalability of acrylated vegetable oil-based polymers.

3.5. Polyurethanes

Bio-based polyurethane coatings have attracted considerable attention due to their mechanical durability, strong adhesion, and environmental resistance, making them suitable for automotive, construction, and protective applications [33]. Mechanical and thermal evaluations of polyurethanes derived from plant oils such as palm and castor oils, as well as from epoxidized vegetable oils, have demonstrated performance comparable to conventional petrochemical-based adhesives [33].

3.5.1. Polyol Synthesis Routes

The synthesis of vegetable oil-based polyurethanes typically involves the reaction of polyols with diisocyanates, carried out via either one-step or two-step polymerization routes. The structure of the polyol, particularly its hydroxyl number and molecular weight, critically determines the mechanical strength, reactivity, and viscosity of the resulting polymer [33].

Depending on the polyol source, significant variations in adhesion, thermal stability, and mechanical integrity can be observed [33,34]. For instance, polyurethanes derived from rapeseed oil exhibit enhanced hydrolytic stability, while linseed oil-based polyurethanes offer superior mechanical resilience, both valuable in coating applications.

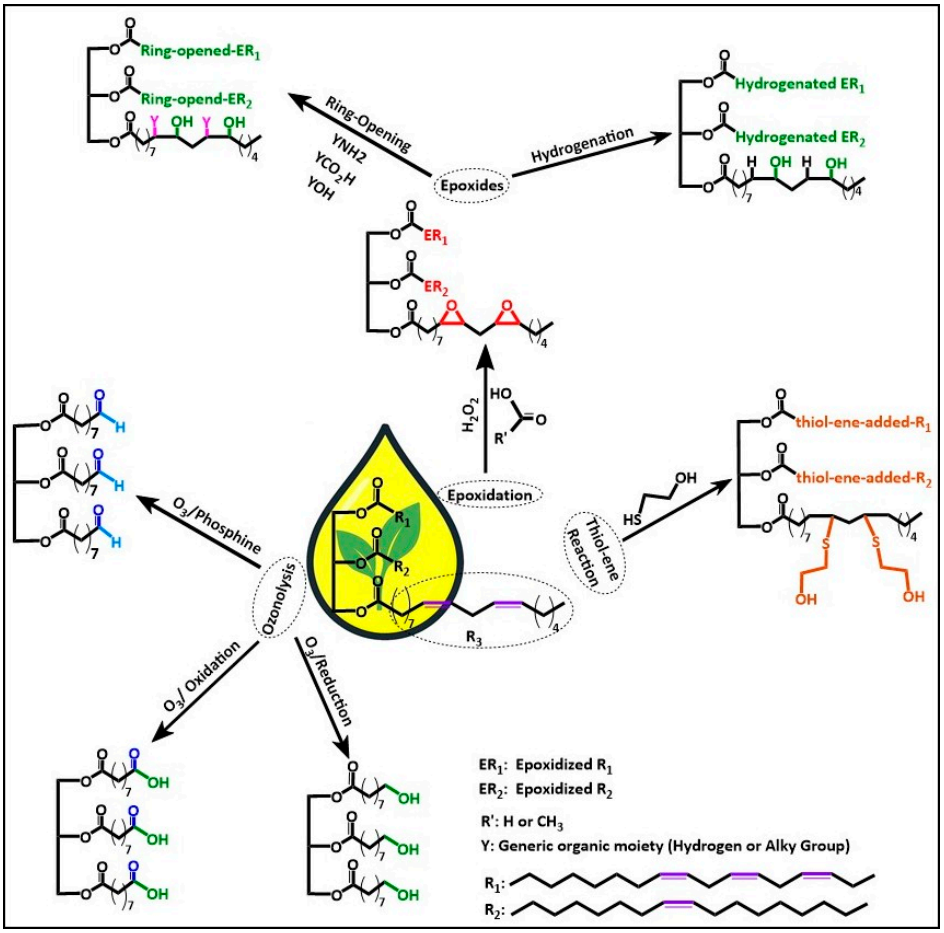
Life cycle assessments consistently highlight the environmental benefits of plant-based polyols, particularly regarding reductions in fossil energy consumption and greenhouse gas emissions. Nevertheless, the limited commercial availability of bio-based isocyanates and occasional reductions in tensile strength compared to petroleum-based alternatives continue to restrict large-scale industrial deployment [34].

Two principal strategies have been developed for synthesizing polyols suitable for polyurethane production from vegetable oils: (a) direct polymerization of functionalized plant oil-derived polyols with diisocyanates and (b) chemical modification of triglycerides to introduce hydroxyl groups prior to polymerization (Scheme 8). Various catalytic and non-catalytic approaches, including acid-catalyzed transesterification, lipase-mediated functionalization, and oxidative cleavage of double bonds, have been explored to optimize polyol performance [3]. Acid-catalyzed transesterification is the most common, while lipase-mediated biocatalysis offers an environmentally friendly alternative, albeit with scalability challenges. Hydroformylation and selective oxidation introduce hydroxyl and carbonyl functionalities while preserving structural integrity, enhancing the crosslinking potential of the resulting polyols [3].

Vegetable oils with a high degree of unsaturation, when subjected to hydroformylation followed by hydrogenation, yield polyols with elevated hydroxyl group concentrations, resulting in denser polyurethane networks. However, such polyols may be less suitable for flexible foam applications, which constitute approximately two-thirds of polyurethane markets [71].

Among chemical modification strategies, epoxidation is widely recognized for enhancing reactivity toward polyurethane synthesis [52,72,73]. As detailed in Section 3.3, epoxidation introduces oxirane rings into triglycerides, facilitating subsequent ring-opening polymerizations or crosslinking reactions that lead to coatings with improved mechanical

strength and adhesion. Additional transformations—including hydrolysis, oxidation, and functionalization—further tailor reactivity profiles [25,74–78].



Scheme 8. Schematic representation of chemical pathways for hydroxyl group insertion into triglycerides.

For example, performic acid epoxidation of Camelina oil followed by methanol-induced ring opening produced polyols with enhanced hydroxyl functionality and rheological properties suitable for polyurethane applications [76]. However, the polyols generated through epoxidation primarily contain secondary hydroxyl groups, which exhibit lower reactivity toward isocyanates compared to primary hydroxyl groups [70].

Ozonolysis followed by hydrogenation offers an alternative route, yielding polyols rich in primary hydroxyl groups [78]. This pathway provides more precise molecular weight control and tunable hydroxyl functionality. Camelina oil-derived mono-, di-, and triols synthesized via ozonolysis have demonstrated improved reactivity profiles and enhanced performance in polyurethane formulations [79]. Nevertheless, careful adjustment of the isocyanate-to-hydroxyl group stoichiometric ratio remains essential to optimize the mechanical performance, flexibility, and durability of polyurethane materials [42].

3.5.2. Performance and Application Examples

Investigations into epoxidized plant oils, particularly from linseed and hemp, have demonstrated that a high oxirane content promotes efficient ring-opening reactions, yielding polyols with tunable viscosities and enhanced crosslinking capabilities [4]. These polyols have enabled the development of polyurethane coatings with excellent mechanical strength, solvent resistance, and film-forming properties [33].

As a practical example, Rajendran et al. synthesized thermoplastic polyurethanes from hemp oil by employing a sequential epoxidation and hydroxylation strategy, with hydroxylation performed in an alcoholic medium containing water, ethanol, and butanol [63]. In a related study, hemp oil was epoxidized and ring-opened with methanol to produce bio-polyols, which were blended with commercial polyols and flame retardants to fabricate rigid polyurethane foams exhibiting flame retardancy and mechanical performance suitable for high-performance applications [80].

Similarly, polyols containing primary hydroxyl groups were synthesized by transesterifying rapeseed oil with triethanolamine. Subsequent functionalization with ε-caprolactone and triethylene glycol generated customized polyols, which were employed in the preparation of polyurethane materials with a 47–59 wt.% bio-based content [81]. Rojek et al. developed flexible polyurethane foams by partially epoxidizing rapeseed oil, followed by oxirane ring opening with diethylene glycol [82]. These bio-polyols partially replaced conventional petrochemical-based triols, resulting in foams with improved cellular structures, reduced environmental impact, and competitive mechanical properties.

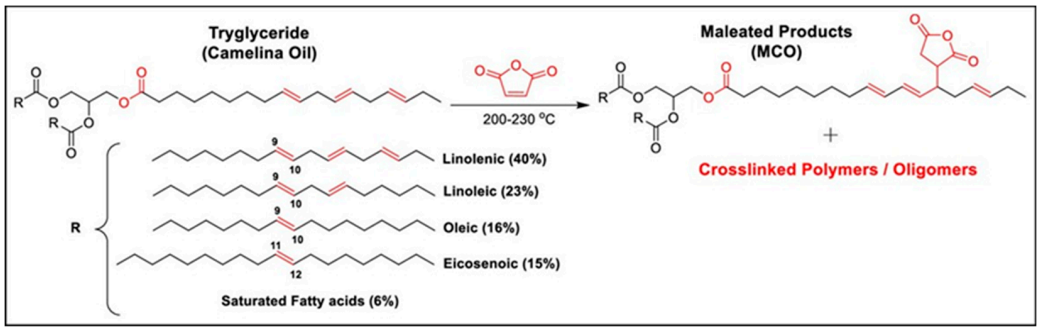
Dworakowska et al. proposed an innovative two-stage approach involving incomplete epoxidation of rapeseed oil followed by microwave-assisted oxirane ring opening. This method generated polyols with distinct hydroxyl values, which were subsequently used in flexible polyurethane foams exhibiting enhanced compressive strength, tensile strength, resilience, and improved cell morphology [83].

3.6. Click Chemistry

Click chemistry has emerged as a powerful and versatile strategy for the efficient and selective functionalization of vegetable oils, offering a compelling alternative to traditional chemical modification methods. These reactions are characterized by high yields, mild reaction conditions, and minimal by-product formation, making them highly compatible with the principles of green chemistry [84]. In the context of vegetable oil-based resins, click reactions allow for the direct attachment of reactive moieties to the unsaturated fatty acid chains of triglycerides. This approach reduces or eliminates the need for extensive pre-functionalization and enables the synthesis of sustainable resins with precisely tailored chemical and mechanical properties.

Among the various click chemistry pathways, thiol-ene coupling has gained particular prominence in the modification of triglycerides due to its rapid reaction kinetics, high chemoselectivity, and compatibility with renewable feedstocks. Through the addition of thiol groups across carbon–carbon double bonds in unsaturated fatty acid chains, this method introduces functional groups such as hydroxyl, carboxyl, and vinyl moieties. These new functionalities act as key intermediates for further polymerizations—particularly in the synthesis of epoxy resins, polyurethanes, and polyesters. Desroches et al. photografted 2-mercaptoethanol onto rapeseed triglycerides in a solvent-free, UV-initiated thiol-ene process, yielding polyols that were subsequently converted into polyurethane elastomers whose thermal behavior rivalled commercial petro-polyols [85]. More recently, Zhang and co-workers formulated a hempseed oil-derived glycidyl epoxy vitrimer and employed UV-triggered thiol-ene surface functionalization to obtain room-temperature-curable, reprocessable coatings with excellent solvent resistance [86].

Diels–Alder cycloaddition has also been reported as an effective click-based functionalization route for triglycerides [87]. For example, in a one-pot, solvent-free Diels–Alder reaction (Scheme 9), maleic anhydride was added to Camelina oil to yield a maleinated resin. The resulting material exhibited enhanced hydrophobicity and improved barrier properties, making it suitable for applications such as paper protective coatings [84].



Scheme 9. Functionalization of Camelina oil using maleic anhydride via a Diels–Alder reaction for paper coatings (adapted from [88], open access).

3.7. Comparative Overview and Auxilary Methods

Beyond their roles in coatings and structural composites, functionalized plant oil networks now underpin a spectrum of advanced technologies. Epoxidized or polyurethane systems furnish scratch-resistant films and high-strength wood or pressure-sensitive adhesives, while foamed tall oil epoxies loaded with ash or clay achieve the low thermal conductivities required of building insulation panels. ZnO-reinforced soybean oil epoxies couple antimicrobial activity with reduced friction for biomedical surfaces, and fibre-reinforced soybean oil resins already meet the dielectric benchmarks of printed-circuit substrates. Tailored chemistries—from cationic soybean oil copolymers to thermoreversible furan–maleimide adducts—deliver shape-memory and self-healing materials that can be reprocessed on demand [89]. Auxiliary process-intensification methods are now entering triglyceride functionalization. Ultrasound, for example, has cut the reaction time in the catalytic transfer hydrogenation of soybean oil at room temperature [90]. Although not yet applied directly to resin curing, such low-energy routes promise efficient complements to established pathways. Taken together, these developments show how judicious molecular modification can extend agronomic feedstocks into application-specific, high-value resin platforms, while new auxiliary techniques offer further efficiency gains.

In broad terms, epoxidation remains the "workhorse" gateway because oxirane groups can be diverted into both acrylate/vinyl and polyol (polyurethane) routes, giving formulators the widest design window. Catalyst-free polyesterification excels where rapid environmental degradation is desired, whereas hyper-branched polyurethane architectures still lead the field in terms of ultimate tensile and thermal performance. Click reactions, finally, inject thermoreversibility, enabling the repair, recycling, or shape-memory behavior now demanded in next-generation coatings and composites [89].

4. Research Gaps, Outlook, and Conclusion

Camelina, hemp, and rapeseed oils present considerable promise for sustainable polymer development due to their regional availability, agronomic resilience, and chemical versatility. Their successful functionalization through methods such as epoxidation, acrylation, and hydroxylation has enabled the synthesis of bio-based polyols with favorable thermal and mechanical properties. However, despite these advances, key challenges remain in achieving consistent reactivity, processing efficiency, and compatibility with conventional polymer systems. Notably, bio-based polyols often exhibit a lower crosslinking density and reduced adhesion strength when compared to petroleum-derived analogues [34,35]. Looking forward, targeted crop-breeding and CRISPR gene-editing programs, such as the creation of high-oleic, yellow-seeded Camelina sativa that boosts desirable unsaturation levels [91], are expected to deliver feedstocks intrinsically optimized for epoxidation and acrylation, thereby narrowing the performance gap with petroleum polyols.

Variability in fatty acid composition and hydroxyl group distribution across different feedstocks further complicates reproducibility and scalability [33]. These limitations are especially evident in epoxidized hemp oil, where the degree of epoxidation—commonly assessed via the iodine value and oxirane oxygen content—directly impacts material performance. Incomplete epoxidation and side reactions may hinder crosslinking efficiency, ultimately compromising mechanical integrity and long-term durability [70]. Emerging enzyme-mediated epoxidation carried out in choline-based deep-eutectic solvents, together with recyclable ion-exchange-resin catalysts, has already achieved near-quantitative oxirane yields while suppressing ring-opening side reactions, promising more reliable crosslinking at scale [92].

While certain systems have demonstrated encouraging results—for instance, the development of hemp oil-based bio-resins via solvent-free epoxidation using peracetic acid and acidic ion-exchange resin catalysts followed by acrylation—overall production is still constrained by high costs. These costs are primarily attributed to complex multistep synthesis pathways and the reliance on expensive catalytic systems [33]. Consequently, future advancements in catalyst design, process intensification, and feedstock optimization will be critical for improving both scalability and economic viability. Parallel advances in continuous-flow millireactors (slug-flow) and microwave-assisted epoxidation are cutting residence times from hours to minutes and lifting oxirane selectivity above 90%, signaling that cost-parity with conventional routes may be reachable within the coming decade [93,94].

Industrial roll-out must also navigate an evolving policy landscape. The EU's 2023 Policy Framework on Biobased and Biodegradable Plastics introduces stricter labelling rules and end-of-life claims, while novel epoxidized intermediates must still undergo full REACH registration, adding time and cost overheads [95]. Brand owners increasingly demand ISCC PLUS certification to verify traceable, low-ILUC rapeseed or camelina feedstocks, which raises auditing and segregation costs [96]. On the economic side, anti-dumping investigations and potential tariffs on epoxy resins in North America have created price uncertainty that keeps bio-based epoxies ~20–30% above petro-equivalent spot prices [97].

Despite these challenges, Camelina, hemp, and rapeseed oils remain highly viable alternatives to petroleum-based polymers when subjected to targeted chemical modifications. Although current limitations in reactivity, crosslinking efficiency, and processability persist, continued innovation in catalyst design, formulation strategy, and structure–property modelling is expected to narrow the performance gap and enable industrial-scale implementation. Integrating dynamic covalent motifs (vitrimers and Diels–Alder bonds) into these oil-derived networks could simultaneously deliver recyclability and self-healing, while open structure–property databases coupled with machine-learning tools stand to accelerate formulation optimization, circular resource utilization, and long-term environmental benefit [98].

Author Contributions: Conceptualization, E.N.; methodology, E.N., P.P. and M.H.; software, E.N.; validation, E.N., M.H. and I.M.; formal analysis, E.N.; investigation, E.N.; resources, I.M.; data curation, E.N.; writing—original draft preparation, E.N. and P.P.; writing—review and editing, M.H., E.J.M. and I.M.; visualization, E.N.; supervision, P.P., M.H., E.J.M. and I.M.; project administration, I.M.; funding acquisition, M.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Technological University of the Shannon (TUS) President's Doctoral Scholarship Fund, grant number PDS2020MH. No external funding was received for this work.

Conflicts of Interest: The authors declare that they have no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

CEA	Canola Oil Esteramide
CPEEA	Canola Oil Polyesteramide
CN	Carbon Number
CO_2	Carbon Dioxide
DB	Number of Double Bonds
DFT	Density Functional Theory
IPN	Interpenetrating Polymer Network
n.d.	Not Determined
UV	Ultraviolet
ZnO	Zinc Oxide

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