

Review Article

Acrylated Biopolymers Derived via Epoxidation and Subsequent Acrylation of Vegetable Oils

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Received 12 November 2021; Revised 27 January 2022; Accepted 14 February 2022; Published 10 March 2022

Academic Editor: Jui-Yang Lai

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Chemically modified vegetable oils have become commercially attractive nowadays because they can be utilized as specialized components for the production of bioplasticizers and biopolymers due to their characteristics as being inexpensive, nontoxic, biodegradable, and renewable products. Due to the presence of unsaturation sites in the vegetable oils, they can be chemically modified and transformed into polymeric monomers such as acrylated epoxidized vegetable oils through well-known processes like epoxidation and acrylation processes. Acrylated epoxidized vegetable oil is a biopolymer that has a multitude of applications and is used mainly as a coating material for plastic, paper, and wood. There is an enormous demand for this biopolymer, and the market growth prospects are huge in some regions of the world. However, there are some challenges in the synthesis of acrylated epoxidized vegetable oils in achieving the performance of similar acrylated polymer derived from petroleum sources. In this paper, the chemical structure, properties, and chemical modifications of different types of vegetable oils were reviewed where the emphasis was given on epoxidation and its subsequent acrylation processes. This paper also highlights four types of epoxidation and their subsequent acrylation processes involving five different vegetable oils.

1. Introduction

Renewable resources are bound to gradually replace petroleum-based feedstock in many chemical industries. Among the renewable resources, vegetable oils (VOs) have drawn a great attention as a popular agricultural product in the industry as they are cheap, nontoxic, biodegradable, and most importantly renewable resources as compared to products from petroleum. Despite their long history of use and benefits, petroleum-based resources have negative environmental consequences due to their high resistance to chemical and biological degradation. Aside from that, the depletion of oil and gas supplies has triggered a search for renewable energy sources [1]. Over the years, many investigations have been carried out to chemically modify VOs with the aim to develop products for industrial application.

Due to the presence of unsaturation in the VOs, the advances in oleochemical technology today allow the VOs to be chemically modified and transformed into polymerizable monomer via epoxidation, metathesis of double bonds, transesterification, etc. [2]. Among them, epoxidation is well known as one of the most popular processes with significant commercial interest because this process can chemically modify the unsaturation presents in the VOs into epoxides. These epoxidized VOs (EVOs) can be used to make a variety of products such as bioplasticizers and biopolymers [3]. The epoxides can be further modified through acrylation, which is an epoxide ring-opening process, to produce acrylated epoxidized VOs (AEVOs) that have an extensive application in the fields of UV-curing coatings, biodegradable foam, and composite materials [4]. In this study, emphasis will be placed on the chemical modification of VOs via epoxidation

followed by the acrylation process.

Although there have been many studies on the synthesis and characterization of AEVOs and their applications in biopolymers or radiation curable coatings, the studies were mainly focused on the experimental synthesis of different type of AEVOs under different operating conditions that produce the best AEVOs with desired properties. Unfortunately, reviews that compare the performance and development of each synthesized AEVO for use in biopolymers were very limited. Thus, this paper does not only summarize the chemical structure, properties, and chemical modifications of VOs with significant attention to the main processes of producing AEVOs from different VO resources via epoxidation and subsequent acrylation but also discusses the global usage of VOs and the market demand for AEVOs.

2. Vegetable Oils: Their Properties and Global Usage

In the past century, VOs have always been an important natural resources in food industries. Approximately 80% of the VOs are utilized for food, while the share is taken up by the industrial sectors. It is useful in cooking and as a source of energy for human body due to their high nutritional level. Slowly, researchers and scientist started to investigate and develop the use of VOs as a feedstock for different kind of nonfood applications in producing useful products due to their inherent biodegradability, low cost, societal favorably advantages, and availability [2]. Another reasons for the rapid expansion of market for VOs in industrial applications are the results of the environmental issue, the depletion of nonrenewable resources, and waste disposal problem [2]. In spite of its advantages, especially for nonfood application, VOs have shown to be brittle, have escalated vapor permeability, and reduced heat distortion temperature which restricts its use commercially compared to synthetic products [5]. Therefore, a challenge imposed is to produce bio-products that are of equal in quality and integrity as synthetic products in terms of lower cost and higher volume without compromising its benefits [6].

2.1. Properties of Different Vegetable Oils for Nonfood Application. Table 1 has listed the iodine value (IV), acid value (AV), and oil content of commonly used vegetable oils around the globe [7–11]. AV is used to determine the amount of potassium hydroxide needed to neutralize the free fatty acid (FFA) content in 1 g of VOs. In other words, it is to determine the amount of FFA in the oils. Each unit of AV is normally equivalent to 0.503% of FFA, meaning that the value is twice of its FFA concentration [7]. For oil content of VOs, a high percentage of oil content indicates that the VOs are suitable as a feedstock in oleochemical industries.

One of the important characteristic of VOs is the IV. It is the parameter that is used to determine the relative degree of unsaturation in oils and fats. By using Wij's method, IV shows the amount of iodine (in grams) that is absorbed by 100 g of oils in the test. A higher IV indicates that there is higher number of double or triple bond in the VOs, thus

TABLE 1: Iodine value, acid value, and oil content of common vegetable oils [7–11].

Vegetable oil	Type	Iodine value (IV) (g I ₂ /100 g oil)	Acid value (AV) (mg KOH/g oil)	Oil content (% w/w)
Soybean	Edible	120-141	2.72	18-23
Palm	Edible	50-55	0.05	45-55
Castor	Nonedible	83-86	1.15	30-35
<i>Jatropha</i>	Nonedible	113-216	2.37	40.03-48.37
Linseed	Edible	170-204	0.80	30-40
Corn	Edible	127-133	—	—
Cottonseed	Edible	98-118	—	—
Olive	Edible	80-88	—	—
Sunflower	Edible	118-141	—	—

higher unsaturation level. In other words, it shows the potential of VOs to go through chemical modification in oleochemical industries for a wider variety of application.

2.2. Global Use of Vegetable Oils. VOs have become one of the global topics of interest mainly due to the rising global demand to increase global wealth and rising awareness of health issue related to fatty acids, as well as increasing international concerns over the effects of deforestation on environment [12]. Thus, VOs are being utilized for both food and industrial use. For food use, soybean oil, rape and mustard oil (including canola oil), palm oil, and sunflower oil accumulated a global VO consumption of more than 70% during the 2000s. While for industrial use, the main VOs being focused on the global market are soybean oil, rapeseed oil, and palm oil, which also accumulated more than 70% of global VO consumption at the same time [13]. The global use of VOs in food can be categorized into six elements: feed, seed, waste, processing, food, and other uses. Other usage include manufacturing of nonfood uses such as biofuel, heating oil, and oleochemicals, where oleochemicals involve plastics, cleaning agents, soaps, cosmetics, alkyd resin, textile, lubricants, and many more [14]. The demand for edible VOs mainly increased in the Americas, Asia, and Europe regions. In terms of GDP, the soybean oil had a real GDP per capita of more than 15,000 US dollar in high income countries while 4,000-14,000 US dollar in middle-high income countries. On the other hand, the per capita consumption of nonedible soybean oil improved in middle income countries at around 1,000-3,999 US dollar [13].

3. Chemical Modifications on Vegetable Oils

3.1. Significance of Chemical Modifications. The modification techniques on VOs have been developed throughout the years to investigate the application of VOs in as much field and industries as possible, at the same time to replace the use of petroleum-based by-products that are both economically and environmentally bad [3]. Chemical modifications are normally conducted on the carboxyl and carbon-

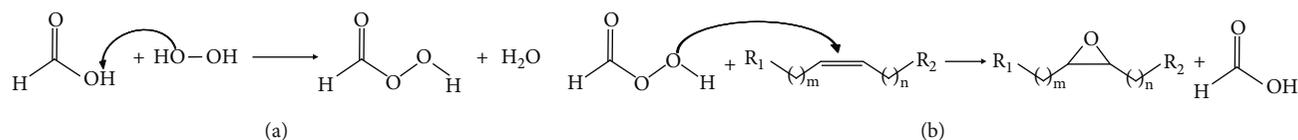


FIGURE 1: Conventional epoxidation process with formic acid and hydrogen peroxide [18].

carbon double or triple bonds available in the triacylglycerol (TAG). Therefore, the unsaturated fatty acids in the VOs act as an important role to react with various chemicals for better properties of product. Chemical modifications are and will be very important in the oleochemical industries in the future for a long period of time. This is because the development on sustainable natural resources such as VOs must be done as wide and as more as possible in order to catch up the continuously increasing demand by human. Chemical modifications not only improve the stability of oils but also provide adequate reactivity to form chemical linkages with other polymer chains that are useful as raw material for a variety of applications.

3.2. Application of Chemically Modified Vegetable Oils and Their Derivatives. The application of modified VOs highly depends on the modification processes conducted on them. There are two reactions that can be done on raw VOs, which are reaction of the carboxyl group and reaction of fatty chain. In the reaction of the carboxyl group, VOs react with methanol to form biodiesel. The crude glycerol by-products formed can then undergo acetalization, oxidation, oligo or polymerization and esterification, hydrogenolysis, glycerolysis, dehydration, and transcarbonation to produce different types of solvents, surfactants, polymers, tanning agents, additives, stabilizers, lubricants, and monomers. On the other hand, the reactions on fatty chain of VOs include epoxidation, metathesis, dimerization, oxidative cleavage, and hydroformylation to produce a variety of emulsifiers, polymers, oleochemicals, agrochemicals, fragrance, pharmaceuticals, plasticizer, polyesters, and polyamides [15]. The EVOs can be further modified via acrylation, methacrylation, or hydroxylation to produce various range of thermosets in the application of coatings, biopolymers, composites, and many more [16]. Also, modified vegetable oils could be used to improve the efficiency of the fabrication process of linoleum floor cloth and to synthesize new polymers that were appropriate for liquid molding [2].

4. Epoxidation of Vegetable Oils

Epoxidation is the process of reacting the peroxy acid with alkene double bonds in the VOs to produce an epoxide functional group. There are four common methods distinguished by the choice of catalysts for the epoxidation of VOs which are Prilezhaev reaction (conventional), acid ion exchange resins (AIER), chemoenzymatic epoxidation, and metal-catalyzed systems.

4.1. Conventional Epoxidation Process. Among them, conventional method is mostly used worldwide due to its easy

and cheap operations. The Prilezhaev reaction, which was first reported in 1909, utilizes the peroxy acid as the oxygen carrier that is formed by reacting organic acid with hydrogen peroxide [17]. During the process, hydrogen peroxide will donate an oxygen element to the organic acid to produce peracid and water, as shown in Figure 1(a). Then, the extra oxygen in the peracid will be consumed by the double bond of VOs to produce an epoxide group, while the original organic acid will be produced again for further generation of another peracid, as shown in Figure 1(b) [18]. The generation of peracid is a reversible reaction and the rate limiting step of the whole process [18]. Therefore, a catalyst in the form of strong mineral acids such as sulphuric acid is normally used to enhance the rate of peracid generation. As compared to a cheaper acetic acid, formic acid has the advantages of being highly electrophilic, allowing it to have higher reactivity to form performic acid without the need of catalyst. Besides, acetic acid has a strong and smelly odour that could be harmful to human when being inhaled.

4.2. Acid Ion Exchange Resins (AIER). In industrial level, the epoxidation processes of VOs have been carried out by the reactions of carboxylic peracids similar to conventional method, but in the presence of mineral acids or strongly acidic ion exchange resins (AIER) [19]. Instead of using homogeneous catalyst, AIER are mainly used for epoxidation on a large scale that is realized in a batch [20]. The use of AIER is able to improve the selectivity of transformation to an epoxy compound through a decrease of opening rate of formed oxirane ring, especially to glycols and glycol monoesters. While having a similar main epoxidation mechanism as conventional method, the use of AIER leads to the happening of several side reactions that always involve a ring opening as shown in Figure 2 [17]. The two major side reactions are the hydrolysis leading to glycols and the acylation to hydroxyl esters [21]. In order to limit the effects of the side reactions, neutralization of postreaction solutions is normally conducted with 10% sodium hydroxide, sodium bicarbonate, or washed with warm water until acid free [21–23].

4.3. Chemoenzymatic Epoxidation. As compared to conventional and AIER method, chemoenzymatic epoxidation is relatively new that uses a small amount of free fatty acids. Chemical method has the disadvantage of acid-catalyzed side-reaction of ring opening that results in several by-products [24]. By using chemoenzymatic method, this issue can be avoided with the reactions in solvents such as toluene [25]. In this method, the peracid transferring oxygen to the double bonds is formed by hydrogen peroxide and fatty acids instead of organic acids, and the reaction is catalyzed

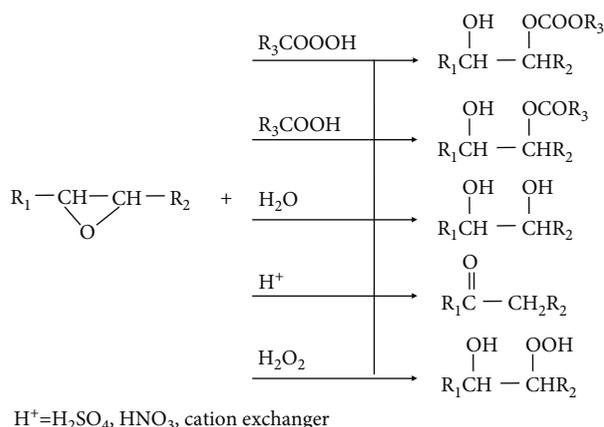


FIGURE 2: Side reactions of epoxidation in the presence of acidic ion exchange resins [19].

by lipase. However, the inactivation of the enzyme by hydrogen peroxide seems to be a major problem for the method. In order to minimize the disadvantage, optimization on reactor design, feed distribution of hydrogen peroxide, solvent choice, and several other factors are needed [26]. The reaction system of chemoenzymatic epoxidation is shown in Figure 3 [27]. The reaction consists of an aqueous phase containing hydrogen peroxide, an organic phase containing solvent, triglycerides, fatty acid, and immobilized enzyme as solid phase [27]. The double bonds can be epoxidized by the peracid formed in the organic phase but decomposition may occur at elevated temperatures. Although lipases are normally used to catalyze hydrolysis of triglycerides and interesterification, the comparatively low water content in organic phase is not suitable for hydrolysis [28, 29]. Thus, the enzyme-recycle reactor system must be optimized to separate the aqueous hydrogen peroxide solution from the enzyme that could be oxidized and deactivated to allow more defined sample in the organic phase [27].

4.4. Metal-Catalyzed Systems. The final epoxidation method is through metal-catalyzed systems. Among the four catalyst types, metal-catalyzed system is the most complicated process as there is a variety of metal catalyst that is viable for the synthesis of the oxirane groups on VOs. The metals that are used as catalysts can be categorized into heterogeneous systems that use zeolites and hydrotalcites as catalysts, homogeneous catalysts attached to solid supports, and soluble metal oxides such as polyoxometalates, peroxotungstates, peroxomolybdates, and methyltrioxorhenium [30]. This allows a wide possibility and choice for the selection of suitable metal catalysts to achieve optimized epoxidation of VOs. In heterogeneous system for epoxidation, the most common mineral-type catalysts are zeolites and hydrotalcites [31–34]. Four-coordinate titanium centers that are featured in microporous siliceous framework are the most commonly used zeolites [35]. Such zeolites are most reactive toward terminal alkene [36]. However, such systems may lead to decomposition of sensitive products when processed at elevated temperatures. Thus, zeolites are normally used for the production of small and stable epoxides [30]. In con-

trast, hydrotalcite systems have wider application due to better reaction with wider variety of substrates [37]. The usual hydrotalcite used is polynuclear-alumina clays [38]. Alumina sources can absorb hydrogen peroxide onto the surface and form an active oxidant for the epoxidation of unfunctionalized alkenes in low to modest yields at ambient temperatures [39]. However, the disadvantage of using metal-catalyzed systems is definitely the increase the production cost of the epoxidation process that is not commonly an option for industrial scale.

5. Acrylation of Epoxidized Vegetable Oils

Acrylation process is one of the reactions that is used to further modify the EVOs chemically to produce more value-added products. Bio-based polymers and resins that can be produced by these AEVOs are attracting a great deal of interest in both research and industrial applications because such biopolymers have many advantages as compared to the conventional petroleum-based polymers [40]. They are biodegradable, renewable resources, and cheaper as a raw material. Besides having benefits to replace petroleum-based polymers, these AEVOs can also be further treated by UV curing to improve their properties in curing and coating industries.

5.1. Acrylation with Acrylic Acid. AEVOs can be successfully synthesized by the reaction between EVOs and acrylic acid in the presence of catalyst and inhibitor. In the reaction, the epoxy groups (oxirane rings) will react with the carboxylic acid groups in the acrylic acid to form an ester. By taking triethylamine (TEA) as a catalyst example, an acrylate anion is produced by the interaction of acrylic acid with TEA as shown in Figure 4 [17]. The hydrogen from acrylic acid is removed as the cation and react with TEA to form triethyl-ammonium. The carbons in the epoxide group comprise reactive electrophiles as a substantial ring strain is relieved when the ring opens upon the nucleophile attack. The acrylate anion acts as the nucleophile to attack the carbon in the epoxy and produce the alcoholate anion. The proton from the amine then transfers to the alcoholate anion and completes the reaction with the formation of epoxy acrylates and reformation of TEA catalyst. The reaction is repeated until all epoxy groups are completely reacted [17]. The acrylation reaction is monitored by measuring the AV of the reaction matrix. The AV and oxirane oxygen content (OOC) will decrease with time as an indicator of the consumption of acrylic acid and the opening of epoxy groups.

5.2. Selection of Catalysts and Inhibitor. The catalyst is used to speed up the reaction between carboxyl groups of acrylic acid and epoxy groups of EVOs. The most common catalysts that are applied by researchers are the TEA and triphenylphosphine oxide. Despite being the most common catalysts, they need to be handled with extra precautions due to their high oral and inhalation toxicity. Thus, an alternative catalyst, namely, AMC-2 that is only applied by a few researches, is also ideal for the process. It is a chromium-based activated metal catalyst that contains a solution of 40-60% chromium

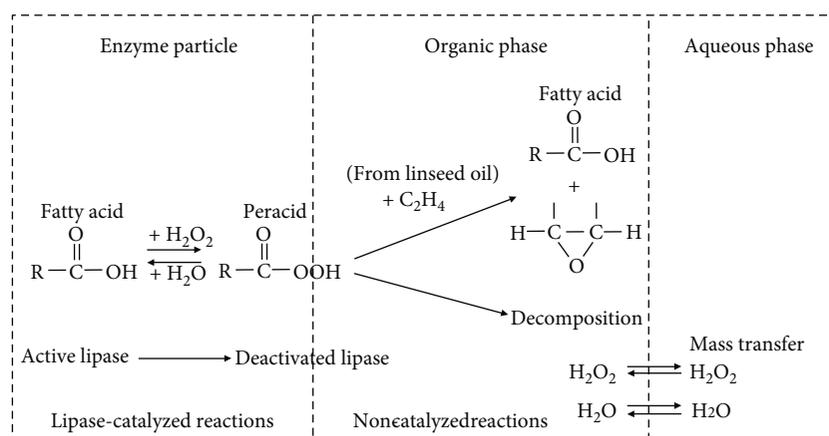


FIGURE 3: Reaction of chemoenzymatic epoxidation [27].

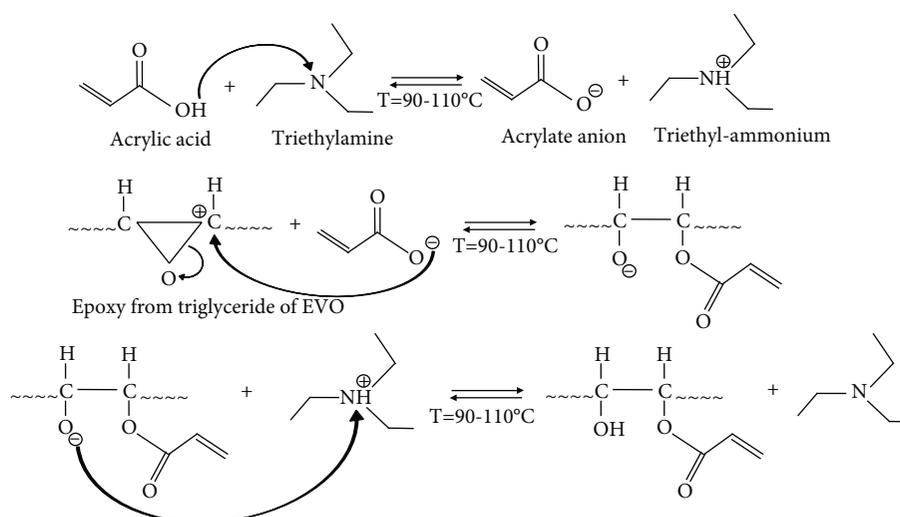


FIGURE 4: Reaction mechanism of acrylation process [17].

(III) 2-ethylhexanoate in a mixture of di-(heptyl, nonyl, undecyl)-phthalates. With a higher safety level, AMC-2 is found to be extremely effective in accelerating the acrylation reaction as well as in inhibiting any homopolymerisation reaction [41]. On the other hand, inhibitor is used to avoid any free radical initiated by polymerization through the acrylic groups [17]. The most common inhibitors are hydroquinone and 4-methoxyphenol. Their impacts in the reaction are almost equivalent to each other.

5.3. Market for Acrylated Epoxidized Vegetable Oils. In evaluating the feasibility of a research, one of the most important element to be considered is the market and demand for the specific items in Malaysia or even worldwide. In fact, Malaysia has been the world's second leading exporter of palm oil after Indonesia with a market share of 60% which palm oil is one of the major sources of vegetable oil worldwide second only to soybean oil. Up to date, palm oil production is around 17.73 million tons in Malaysia, accounting for 11% of the world's oil and fat production and 27% of exports [42]. Thus, the synthesis of AEVOs would undoubtedly use palm oil as the primary source. On the other hand, the

depletion of fossil fuels or petrochemicals would lead to the increase in price in the near future. As a reliable alternative, VO's such as palm oil have a competitive price of around RM15 per kg that is lower than the RM40 per kg of petrochemicals. While for the market of acrylated epoxidized palm oil in Malaysia as shown in Figure 5, 62% of the production is used for industrial coatings, followed by 25% for opto-electronics, 6% for printing inks, 5% for overprint varnishes, and 2% for adhesives [43].

In Europe, market for wood coatings and graphic arts including overprint inks and varnishes accumulates for about 80% of demand. In Asia, excluding China, radiation curable resists, color filter resists, and film resists are in the 30-40% of total market for radiation curable products. Last but not the least, in China, around 60% of the total market is contributed by the radiation curable coatings for plastics, paper, and wood [44].

5.4. Acrylation of Epoxidized Soybean Oil. A few researchers have studied the synthesis of acrylated epoxidized soybean oil (AESO) for the application in UV-curable coatings and free radical polymerization. The important parameters that

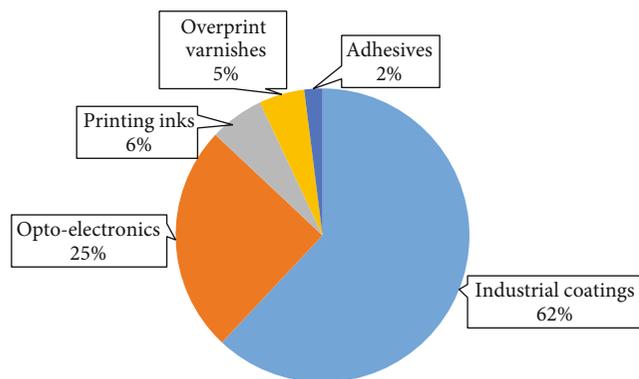


FIGURE 5: Market of acrylated epoxidized palm oil in Malaysia [43].

are extracted from the papers are shown in Table 2 [1, 4, 45–47]. The molar ratio of ESO to acrylic acid ranged from 1:0.165 to 1:10 which was a very large different in amount of acrylic acid being used. The reaction temperature was between 80 and 120°C depending on the type and amount of epoxidized soybean oil (ESO), catalyst, and inhibitor used. The reaction time was conducted between 6 and 40 hours, where the optimum reaction time was around 6 hours and the remaining time was used to ensure that the reaction between acrylic acid and epoxy groups had completed. Only one paper stated that they had successfully convert 95% of ESO into AESO [4]. OOC of ESO that was around 6.2% was found to be reduced to 0.01%, indicating the complete ring opening of the epoxy groups. Table 3 presents the FTIR analysis of ESO and AESO that are conducted by Behera and Banthia [45]. The diminished of the oxirane group at 912 cm^{-1} and 882 cm^{-1} in AESO indicated that the oxirane groups had been reduced. The success of acrylation was further confirmed by the appearance of the acrylate groups at 1637 cm^{-1} , 1461 cm^{-1} , and 1406 cm^{-1} .

5.5. Acrylation of Epoxidized Palm Oil. In Malaysia, the most popular VO to be applied in industries are certainly none other than palm oil. Due to its abundant source, palm oil has been widely applied in acrylation process to produce UV-curable coating, promising biopolymer, and nanocomposite materials. According to some studies, refined palm olein is preferred over unrefined palm oil because it has a slightly higher iodine value, allowing for a greater degree of modification. However, the acrylation process with acrylic acid is still the same for both raw materials. As shown in Table 4, the applied molar ratio of epoxidized palm oil (EPO) to acrylic acid ranged from 1:1.5 to 1:2.6 with the reaction temperature of 80–120°C as well [40, 41, 48–50]. Kosheela et al. found that a synthesis at molar ratio of 1:1.5, 120°C, and 2 hours produced the highest conversion rate at 90.69% for palm olein [41]. From the available information, it was shown that palm olein tends to have a slightly higher conversion rate from epoxidized palm olein oil. Acrylation process was proved to be a success with the reduction of OOC from 3.22% to 0.2%. According to FTIR spectra in Figure 6, the appearance of the hydroxyl group (-OH) at 3470 cm^{-1} was due to the opening of epoxy ring [40]. The

epoxy ring stretching (C-O-C) at 1240 cm^{-1} and 835 cm^{-1} diminished after the synthesis of AEPO. On the other hand, the appearance of the acrylate groups ($\text{CH}_2=\text{CH}$) at 1636 cm^{-1} , 1406 cm^{-1} , and 810 cm^{-1} indicated that the AEPO was successfully produced. Most of the papers found were focusing on the investigation of the properties of UV-curable coating produced from AEPO. Thus, a thorough comparison of operating conditions on the product yields could hardly be found.

5.6. Acrylation of Epoxidized Castor Oil. The acrylation process of epoxidized castor oil (ECO) is less popular, and only two papers could be found. The researchers synthesized the acrylated epoxidized castor oil (AECO) to compare the characteristics among different modification process. The optimum operating conditions from both papers were identical, which was an oil to acrylic acid of 1:5.5 at a reaction temperature of 60–70°C and time of 2.5 hours [51, 52]. Unfortunately, the conversion yield of AECO was not reported. A slight decrease in OOC from 6.5% to 5.2% confirmed the ring-opening process of the oxirane groups. From the FTIR spectrum of AECO in Figure 7, OH stretching could be identified at 3395 cm^{-1} while acrylic groups at 1637 cm^{-1} , 1459 cm^{-1} , and 1406 cm^{-1} . However, the peak at 840 cm^{-1} depicted that the epoxide groups were retained after the acrylation, showing that 2.5 hours were too short for a complete acrylation process [52]. The mechanical properties of ECO, AECO, and AECO nanocomposites prepared from organo-modified montmorillonite (AECO/OMMT) were studied by Paluvai et al. [51]. It could be seen from Table 5 that acrylation process had improved the tensile and flexural properties of AECO, and the properties could be further enhanced through the synthesis of nanocomposites. Thus, the improved curing characteristics allow AECO to be further applied in coating industries [51].

5.7. Acrylation of Epoxidized Linseed Oil. Linseed oil, also known as flaxseed oil, is chemically modified for value-added products due to its high unsaturation level as it is one of the oils that has the highest IV, thus showing its potential for chemical modifications. Acrylated epoxidized linseed oil (AELO) is being synthesized for biopolymeric and wood coating applications as well. In the acrylation process of epoxidized linseed oil (ELO), a molar ratio of 1:1 was reported to be reacted at the temperature of 75°C for 2–6 hours [53, 54]. This was by far the lowest reaction temperature reported as compared to other VOs, which might due to the properties of linseed oil. However, the conversion rate of ELO to AELO and change in OOC and AV were not reported. It is believed that ELO might have the highest OOC, which is around 9% due to high IV. Although OOC was not reported, the evidence in acrylation process could be provided by FTIR spectrum. The FTIR spectrum shown in Figure 8 confirmed the formation of AELO via the peaks at 3455 cm^{-1} (-OH) and the acrylate groups at 1406 cm^{-1} , 984 cm^{-1} , and 810 cm^{-1} ($\text{CH}=\text{CH}_2$). When most of the oxirane groups were converted to the acrylate groups, some of them still remained after acrylation, which could be identified at the remaining signal at 830–850 cm^{-1} [54].

TABLE 2: Important parameters for acrylation of epoxidized soybean oil [1, 4, 45–47].

Catalyst/inhibitor (% w/w of reactants)	EVO: acrylic acid	Temperature (°C)	Reaction time (h)	Conversion (%)	OOC (wt %)	AV (mg KOH/g)
1.5% triphenylphosphine oxide/0.5% p-tert-butylcatechol	1:0.8	120	6	95	—	5
1% triphenylphosphine/0.03% butylated hydroxy toluene	1:2	90-95	6	—	6.4 to 0.012	1.0 to 1.15
Triethylamine/hydroquinone	1:0.165	80	20	—	—	6.2
-/hydroquinone	1:10	110	7	—	—	—
1.0% triethylamine/0.5% hydroquinone	1:4	110	40	—	6 to 0.1	108

TABLE 3: FTIR absorption peaks of ESO and AESO [43].

ESO		AESO	
Absorption peak, cm ⁻¹	Functional group	Absorption peak, cm ⁻¹	Functional group
3478	OH str (weak)	3470	OH str (strong)
2944	CH str	2927, 2856	CH str
1740	C=O str	1740	C=O str
—	—	1637	H ₂ C=CH str
1378	CH sym band	1378	CH sym band
1282	C-O str	1270	C-O str
1142	C-C-O str	1189, 1057	C-C-O str
912, 882	C-O-C oxirane groups	967, 810	C-C-O Asy band
1468	CH scissoring band	1461	CH scissoring band
—	—	1406	H ₂ C=CH scissoring band for terminal alkene

TABLE 4: Important parameters for acrylation of epoxidized palm olein/oil [40, 41, 48–50].

EVO	Catalyst/inhibitor (% w/w of reactants)	EVO: acrylic acid	Temperature (°C)	Reaction time (h)	Conversion (%)	OOC (wt %)	AV (mg KOH/g)
Palm olein	1% AMC-2/0.1% hydroquinone	1:1.5	120	2.25	90.69	—	—
Palm oil	1% triethylamine/1% 4-methoxyphenol	1:1.52	110	16	82	3.0 to 0.2	51 to 10.2
Palm olein	0.25% triethylamine/0.25% 4-methoxyphenol	1:2	<130	21	86.64	3.22 to 0.46	81.45 to 18.11
Palm oil	Triethylamine/hydroquinone	1:2.2	80	14	—	—	—
Palm olein	—	1:2.6	110-120	34	—	0.18	47.78

5.8. *Acrylation of Epoxidized Jatropha Seed Oil.* *Jatropha* seed oil is another nonedible oil that is renewable and sustainable to produce vegetable oil-based epoxy and epoxy acrylate as a raw polymeric material [55]. Due to the presence of toxic compounds named phorbol ester, *Jatropha* seed oil could not be used for cooking [17]. Thus, the potential of modifying *Jatropha* seed oil for the coating industry must be investigated to utilize these natural resources. Aside from palm oil, *Jatropha* seed has become one of the most important crops in Malaysia within the palm oil and rubber industries [17]. In this acrylation process of epoxidized *Jatropha* seed oil (EJO), the molar ratios are around 1:1 to 1:1.5 to obtain highest possible yield (82.44%). The reaction temperature is at 110°C for a duration of 6 hours. EJO has an

OOC of 5%, which is reduced to around 0.17% after the oxirane ring-opening process. The decrease of AV from 27 mg KOH/g to 4.42 mg KOH/g shows that the acrylic acid is being consumed [17, 55]. For the FTIR spectrum in Figure 9, the hydroxyl group (-OH) was identified at 3473 cm⁻¹ due to the ring-opening reaction of epoxide by catalyst reaction. 3006 cm⁻¹ at *Jatropha* seed oil spectrum belonged to the unsaturated double bond of fatty acids. The synthesis of acrylated epoxidized *Jatropha* seed oil (AEJO) was confirmed by the acrylate double bond (CH=CH₂) at 1636 cm⁻¹ and 1618 cm⁻¹. Last but not the least, a small peak of the epoxide group at 830 cm⁻¹ indicated that not all epoxy groups have been consumed during the acrylation process [55].

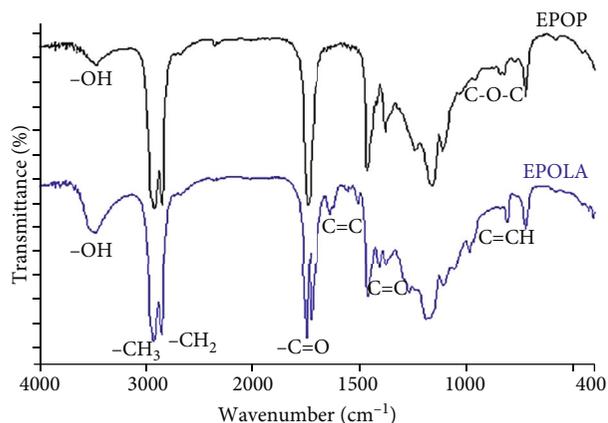


FIGURE 6: FTIR spectra of EPOP (EPO) and EPOLA (AEPO) (from Ashraf et al. [40], adapted).

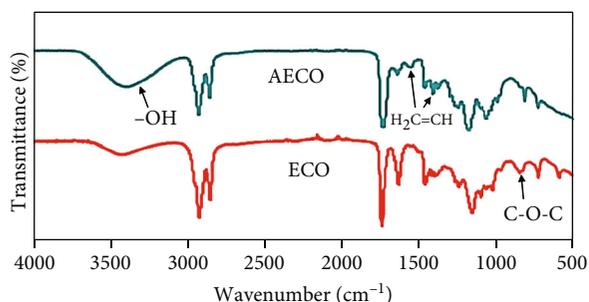


FIGURE 7: FTIR spectra of ECO and AECO (from Sudha et al. [52], adapted).

TABLE 5: Mechanical properties of ECO and AECO and its nanocomposites [51].

Bio-based epoxy system	Tensile strength (MPa)	Tensile modulus (MPa)	Flexural strength (MPa)	Flexural modulus (MPa)
ECO	20.1 ± 1	664 ± 19	38.8 ± 2.6	820 ± 30
AECO	26.2 ± 1.3	908 ± 29	50.4 ± 2.7	1080 ± 33
AECO/0.5%C30B	30.8 ± 2	1063 ± 26	56.1 ± 1.8	1257 ± 28
AECO/1% C30B	32.4 ± 1.5	1107 ± 32	59.4 ± 4.2	1309 ± 40
AECO/2% C30B	30.6 ± 1.2	1154 ± 30	54.2 ± 2.5	1381 ± 37
AECO/3% C30B	27.1 ± 1.9	1253 ± 36	52.2 ± 1.2	1485 ± 50

6. Characterization of Acrylated Epoxidized Vegetable Oils

6.1. Yield. In order to identify the feasibility of chemical modification on AEVOs, the most important parameter should be none other than the yield of AEVOs from EVOs. This is because the industries always focus on producing a product that is cost effective and have high yield percentage. In calcu-

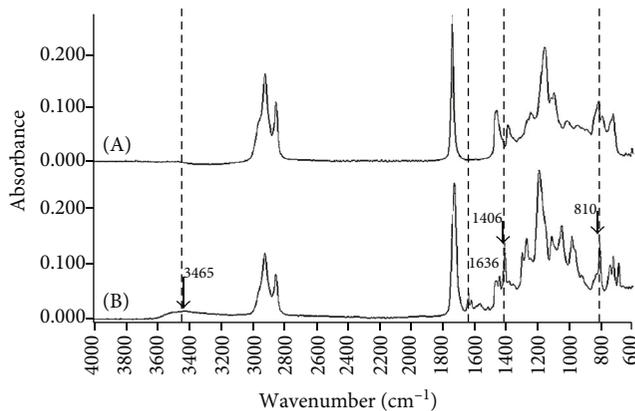


FIGURE 8: FTIR spectra of ELO and AELO (from Wuzella et al. [54], adapted).

lating the yield percentage, the experimental and theoretical mass of AEVOs should be determined. The theoretical mass of AEVOs can be calculated based on the mass balance concept where $\text{AEVO (g)} = \text{EVO (g)} + \text{Acrylic acid (g)} - \text{Spent acid (g)}$. On the other hand, the experimental mass of AEVOs could be measured and recorded directly by using an electric balance. The yield can then be calculated by Equation (1). With reference to the results obtained from researchers on different AEVOs, the desired AEVOs yield should at least 80-85% in order to be feasible for nonfood application to achieve both requirements of cost effective and large production rate.

$$\text{Yield (\%)} = \frac{\text{AEMO}_{\text{experimental}}}{\text{AEMO}_{\text{theoretical}}} \times 100\%. \quad (1)$$

6.2. Iodine Value (IV). IV is another important parameter that is involved in the characterizations of AEVOs as it determines the relative degree of unsaturation in oils and fats. In other words, IV indicates the potential of VO to be chemically modified. IV should be determined for each oil sample before and after epoxidation and acrylation processes. IV can be determined by using the common Wijs' method [7]. Firstly, 0.4 g of oil sample is mixed with 20 mL of carbon tetra chloride in a conical flask. Then, 25 mL of Dam's reagent is added to the flask using a pipette. Stopper is then inserted, and the content is vigorously swirled. The flask is then placed in the dark for 2 hours and 30 minutes. After the duration, 20 mL of 10% aqueous potassium iodide and 125 mL of water are added. The content is titrated with 0.1 M sodium-thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) solutions until the yellow color almost disappeared. Few drops of 1% starch indicator are added, and the titration is continued by adding $\text{Na}_2\text{S}_2\text{O}_3$ dropwise until blue coloration disappeared after vigorous shaking. The procedures are used for blank test and oil samples. IV is calculated by Equation (2), where C is the concentration of $\text{Na}_2\text{S}_2\text{O}_3$, V_1 is the volume of $\text{Na}_2\text{S}_2\text{O}_3$ used for blank (mL), V_2 is the volume of $\text{Na}_2\text{S}_2\text{O}_3$ used for determination (mL), and W is the mass of sample (g).

$$\text{IV} = \frac{12.69 \times C(V_1 - V_2)}{W}. \quad (2)$$

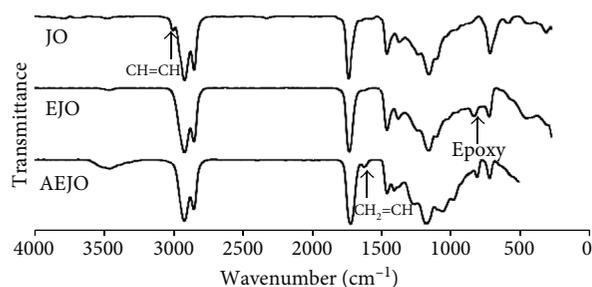


FIGURE 9: FTIR spectra of Jatropa oil, EJO, and AEJO (from Wong et al. [55], adapted).

As compared to the raw VOs, the IV after epoxidation process should decrease due to the formation of the epoxide groups on the double bonds of VOs that reduces the unsaturation level. However, the IV will increase again once the ring opening of the epoxide groups with acrylic acid occurs during the acrylation process. This is because the acrylate groups produced contain double bonds as well, which will increase the unsaturation level of the AEVOs.

6.3. Oxirane Oxygen Content (OOC). The IV determined will be further applied to calculate the theoretical OOC of the samples. OOC determines the amount of oxygen of the epoxy groups available in the sample. This parameter is particularly significant in the verification of the formation and destruction of the epoxide groups. For analysis, the oil samples of EVOs and AEVOs are titrated with hydrobromic acid (HBr) in acetic acid under the conditions defined in AOCS Analysis Method Cd 9-57 [7]. 0.5 g of oil sample will be collected, and 10 mL of glacial acetic acid is added. Before the mixture is titrated with 0.14 N of HBr solution, five drops of crystal violet indicator are added to determine the endpoint of titration, which occurs when the color changes from blue to green. The volume of HBr used will be recorded, and OOC is calculated by using Equation (3), where V is volume of HBr (mL), N is normality of HBr, and W is the weight of sample (g).

$$\text{OOC}_{\text{exp}}(\%) = \frac{V \times N \times 1.60}{W} \times 100\%. \quad (3)$$

The obtained experimental OOC will then be compared with the theoretical OOC by using Equation (4), where IV_o is the initial iodine value of VOs or EVOs, A_o is the atomic weight of oxygen (16), and A_i is the atomic weight of iodine (126.9). The determination of OOC will be repeated for AEVOs.

$$\text{OOC}_t = \frac{IV_o/2A_i}{100 + (IV_o/2A_i) \times A_o} \times A_o \times 100. \quad (4)$$

From the experiment by researchers, the determined OOC for EVOs are around 4.0-6.0% that successfully proved the existence of the epoxide groups in the EVOs after the epoxidation process. For the epoxide ring-opening process, the OOC for AEVOs are expected to drop to almost 0% as reported by the authors. This largely depends on the amount

of acrylic acid used to fully or partially react with the EVOs. 0% OOC will only occur at complete acrylation process where all the epoxide groups are successfully diminished.

6.4. Acid Value (AV). AV determines the amount of acrylic acid remained after the acrylation process. This parameter is only tested in the final product AEVO which is not that particularly important in proving the occurrence of acrylation process. Firstly, 25 mL of acrylic acid and 25 mL of ethanol are mixed in a 250 mL beaker. The resulting mixture is added to 10 g of EMO in a 250 mL conical flask, and few drops of phenolphthalein are added to the mixture. The mixture is titrated with 0.1 M sodium hydroxide (NaOH) to the endpoint when a dark pink color is observed. The volume of NaOH (V_o) in mL will be noted. Free fatty acid (FFA) is calculated by Equation (5), where 100 mL of 0.1 M NaOH = 2.83 g of oleic acid and W_o is sample weight (g). Then, $AV = \text{FFA} \times 2$ [5]. The determination of AV will be repeated for AEVOs.

$$\text{FFA}(\%) = \frac{V_o}{W_o} \times 2.82 \times 100. \quad (5)$$

As reported, the AV should have a drastic decrease after the acrylation process to show that the acrylic acid is being consumed to react with the epoxide groups and form acrylate groups. The calculated AV can also be used to identify the optimum amount of acrylic acid required in the process to avoid excessive usage of acrylic acid, depending on the amount of oil sample used. Once the acrylic acid is completely consumed, the acid value of AEVOs should drop to almost 0 mg KOH/g.

6.5. Fourier Transform Infrared (FTIR) Spectroscopy. The FTIR spectroscopy was applied to identify the functional groups present in the oil samples VO, EVO, and AEVO, which directly confirm whether the epoxidation and acrylation processes are successful. As reported by researchers, the epoxide group was identified in EVO at 845 cm^{-1} showing the formation of oxirane ring in the oil. On the other hand, the OH group should appear at around 3395 cm^{-1} while the acrylate groups at around $1406\text{-}1636 \text{ cm}^{-1}$ in AEVO after the ring-opening process with acrylic acid. Spectrum for the epoxide groups should diminished if the rings have been completely reacted.

7. Major Challenges for Vegetable Oils as Feedstock in Nonfood Application

Although the AEVOs are slowly developed to be produced into biopolymers and some other applications, the major challenges for VO-based polymers to replace the conventional petroleum-based polymers still exist. First and foremost, the performance gap between products produced from both types of polymers is still under review. Although chemical modifications can lead to improvements in the processing properties, thermal properties, and mechanical properties, a comprehensive and straightforward comparison of performance is yet to be done. On the other hand,

due to the application of VOs in food industry, it is already proved by statistics that the annual production of chemicals and materials from VOs is very insignificant with a small figure of 28 million tonnes as compared to the 400 million tonnes produced from petrochemicals, thus making petrochemical a still compulsory resource in the current era.

Another issue that limits the application of VOs for the production of chemicals is the quality control of VOs as the raw materials. This is because the composition of VOs can vary significantly based on a variety of growing factors, including cultivar selection, location, and environmental conditions as well as processing techniques. The energy input and newly generated chemical waste during the synthesis of monomers and polymers by using VOs will be different too. In order to produce a quality product, the quality control of raw materials could not be neglected. Therefore, addressing these concerns requires interdisciplinary efforts, which directly affected the current progress in completely implementing VOs in the nonfood application.

Many researchers have attempted to tackle the performance issues with various strategies in order for the application of AEVOs to be on par with synthetic polymers in the industry. Mixing with other types of polymers or incorporating nanofiller is one of the methods often used to enhance the mechanical and barrier properties of the resulting thermoset polymers [56, 57]. Alternatively, with concerns to thermal stability, the AEVOs with comonomer addition such as 1,6-hexanediol diacrylate and trimethylolpropane triacrylate are able to increase glass transition temperature and thermal degradation temperature [58]. The incorporation of phosphorus-containing chemical reagent into UV-curable AEVOs has shown to have the same improved thermal stability properties with additional advantages of enhanced adhesion and volumetric shrinkage while sustaining its crosslinking density [59]. These properties could also be improved in AEVOs by producing biocomposites with fibers [60]. The ongoing trend in research with regard to the enhancement of AEVOs and growing introduction of “green” materials in formulations presents the possibility in replacing petroleum-based feedstock in the future.

8. Conclusion

In summary, VOs are gaining a lot of attention in manufacturing industry due to its advantages of being environmental friendly, cheap, biodegradable, and renewable leading to abundant resources. By applying chemical modifications on the unsaturated fatty acids in VOs, the properties of VOs can be improved to synthesis a wide variety of products that are useful in the daily lives. Among the four epoxidation methods distinguished by the type of catalysts applied, each of them has particular advantages and disadvantages whether in laboratory or industrial level. The selection of epoxidation method largely depends on the overall design of the process and plant, the characteristics of reactants, economic evaluation within, and many more. After the epoxidation process, the EVOs can be further synthesized into AEVOs, which are the feedstock for the production of radiation curable coatings, biodegradable foam, etc.

If the VO is developed efficiently for manufacturing purpose, it would definitely benefit the environment and the local people by creating job opportunity and alternative resources that are renewable for future application.

Abbreviations

TAG:	Triacylglycerol
AECO:	Acrylated epoxidized castor oil
AEJO:	Acrylated epoxidized <i>Jatropha</i> seed oil
AELO:	Acrylated epoxidized linseed oil
AEPO:	Acrylated epoxidized palm oil
AESO:	Acrylated epoxidized soybean oil
AEVO:	Acrylated epoxidized vegetable oil
AV:	Acid value
ECO:	Epoxidized castor oil
EJO:	Epoxidized <i>Jatropha</i> seed oil
ELO:	Epoxidized linseed oil
EPO:	Epoxidized palm oil
ESO:	Epoxidized soybean oil
EVO:	Epoxidized vegetable oil
FTIR:	Fourier transform infrared
IV:	Iodine value
OOC:	Oxirane oxygen content
VO:	Vegetable oil.

Data Availability

Data are available on request from the authors.

Additional Points

Practical Applications. Vegetable oil-based acrylated epoxidized oils can be used as bioplasticizer and biopolymer for coating of plastic, paper, and wood.

Conflicts of Interest

The authors declare that they have no conflict of interest.

Acknowledgments

This work was funded by the Xiamen University Malaysia Research Fund (Grant no. XMUMRF/2019-C3/IENG/0012).

References

- [1] M. Nagalakshmaiah, S. Afrin, R. P. Malladi et al., “Chapter 9-Biocomposites: Present Trends and Challenges for the Future,” in *Woodhead Publishing Series in Composites Science and Engineering, Green Composites for Automotive Applications*, pp. 197–215, Woodhead Publishing, 2019.
- [2] S. G. Tan and W. S. Chow, “Biobased epoxidized vegetable oils and its greener epoxy blends: a review,” *Polymer - Plastics Technology and Engineering*, vol. 49, no. 15, pp. 1581–1590, 2010.
- [3] V. J. Hattimattur, V. R. Sangale, P. S. Zade, M. B. Mandake, and S. Walke, “Review: epoxidation of vegetable oils,” *International Journal of Trend in Research and Development*, vol. 5, 2018.

- [4] X. M. Chu, S. J. Liu, and F. Q. Zhao, "Preparation of acrylated epoxidized soybean oil with excellent properties," in *Applied Mechanics and Materials*, vol. 662, pp. 7–10, Trans Tech Publications Ltd., 2014.
- [5] A. M. Diez-Pascual, "Antibacterial nanocomposites based on thermosetting polymers derived from vegetable oils and metal oxide nanoparticles," *Polymers*, vol. 11, no. 11, p. 1790, 2019.
- [6] G. Lligadas, J. C. Ronda, M. Galià, and V. Cádiz, "Renewable polymeric materials from vegetable oils: a perspective," *Materials Today*, vol. 16, no. 9, pp. 337–343, 2013.
- [7] U. G. Akpan, A. Jimoh, and A. Mohammed, "Extraction, characterization and modification of castor seed oil," *Leonardo Journal of Sciences*, vol. 8, 2006.
- [8] A. K. M. Akminul Islam, S. R. P. Primandari, Z. Yaakob, N. Anuar, and M. Osman, "The properties of *Jatropha curcas* seed oil from seven different countries," *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, vol. 35, no. 18, pp. 1698–1703, 2013.
- [9] A. Abitogun, A. Jide, J. Arawande, J. O. Alademeyin, and A. Omosheyin, "Effects of phosphoric acid on physico-chemical parameters of soybean oil," *The Internet Journal of Nutrition and Wellness*, vol. 8, no. 2, 2008.
- [10] C. P. Tan and I. A. Nehdi, "The Physicochemical Properties of Palm Oil and Its Components," in *Palm Oil*, O.-M. Lai, C.-P. Tan, and C. C. Akoh, Eds., pp. 377–391, AOCS Press, 2012.
- [11] V. Popa, A. Gruia, D. Raba et al., "Fatty acids composition and oil characteristics of linseed (*Linum usitatissimum* L.) from Romania," *Journal of Agroalimentary Processes and Technologies*, vol. 18, no. 2, pp. 136–140, 2012.
- [12] D. C. Morton, D. F. RS, Y. E. Shimabukuro et al., "Cropland expansion changes deforestation dynamics in the southern Brazilian Amazon," *Proceedings of the National Academy of Sciences*, vol. 103, no. 39, pp. 14637–14641, 2006.
- [13] J. Parcell, "Global edible vegetable oil market trends," *Biomedical Journal of Scientific & Technical Research*, vol. 2, no. 1, 2018.
- [14] S. Appalasami and R. J. de Vries, "The future of palm oil in oleochemicals," *Palm Oil Development*, vol. 14, pp. 18–29, 1990.
- [15] N. Samarth and P. Mahanwar, "Modified vegetable oil based additives as a future polymeric material—review," *Open Journal of Organic Polymer Materials*, vol. 5, no. 1, pp. 1–22, 2015.
- [16] K. Nwosu-Obieogu and U. Kalu, "In situ epoxidation of sesame seed oil for synthesis of a bio-based resin," *European Journal of Sustainable Development Research*, vol. 4, no. 3, p. 4, 2020.
- [17] E. R. J. Taib, L. C. Abdullah, M. M. Aung et al., "Physico-chemical characterisation of epoxy acrylate resin from *jatropha* seed oil," *Pigment & Resin Technology*, vol. 46, no. 6, pp. 485–495, 2017.
- [18] P. T. Wai, P. Jiang, Y. Shen, P. Zhang, Q. Gu, and Y. Leng, "Catalytic developments in the epoxidation of vegetable oils and the analysis methods of epoxidized products," *RSC Advances*, vol. 9, no. 65, pp. 38119–38136, 2019.
- [19] E. Milchert, K. Malarczyk-Matusiak, and M. Musik, "Technological aspects of vegetable oils epoxidation in the presence of ion exchange resins: a review," *Polish Journal of Chemical Technology*, vol. 18, no. 3, pp. 128–133, 2016.
- [20] A. Dinda, A. V. Patwarthan, V. V. Goud, and N. C. Pradhan, "Epoxidation of cottonseed oil by aqueous hydrogen peroxide catalysed by liquid inorganic acids," *Bioresource Technology*, vol. 99, no. 9, pp. 3737–3744, 2008.
- [21] B. Rangarajan, A. Havey, E. A. Grulke, and P. D. Culnan, "Kinetic parameters of a two-phase model for in-situ epoxidation of soybean oil," *Journal of the American Oil Chemists' Society*, vol. 72, no. 10, pp. 1161–1169, 1995.
- [22] E. Milchert and A. Smagowicz, "The influence of reaction parameters on the epoxidation of rapeseed oil with peracetic acid," *Journal of the American Oil Chemists' Society*, vol. 86, no. 12, pp. 1227–1233, 2009.
- [23] Z. S. Petrović, A. Zlatanić, C. C. Lava, and S. Sinadino-vi- Fišer, "Epoxidation of soybean oil in toluene with peroxyacetic and peroxyformic acids — kinetics and side reactions," *European Journal of Lipid Science and Technology*, vol. 104, no. 5, pp. 293–299, 2002.
- [24] E. U. Ikhuoria, R. O. Obuleke, and F. E. Okieimen, "Studies on the kinetics of epoxidation of the methyl esters of parkia biglobosa seed oil," *Journal of Macromolecular Science, Part A*, vol. 44, no. 2, pp. 235–238, 2007.
- [25] M. R. G. Klaas and S. Warwel, "Chemo-enzymatic epoxidation of unsaturated fatty acid esters and plant oils," *Journal of the American Oil Chemists' Society*, vol. 73, no. 11, pp. 1453–1457, 1996.
- [26] A. E. Hagström, U. Törnvall, M. Nordblad, R. Hatti-Kaul, and J. M. Woodley, "Chemo-enzymatic epoxidation – process options for improving biocatalytic productivity," *Biotechnology progress*, vol. 27, pp. 67–76, 2010.
- [27] I. Hilker, D. Bothe, J. Prüss, and H. J. Warnecke, "Chemo-enzymatic epoxidation of unsaturated plant oils," *Chemical Engineering Science*, vol. 56, no. 2, pp. 427–432, 2001.
- [28] M. Martinelle, *Lipases from Candida antarctica and Humicola lanuginosa: Structure Activity Relationships and Applied Catalysis*, Royal Inst. Technol., 1995.
- [29] J. Uppenberg, M. T. Hansen, S. Patkar, and T. A. Jones, "The sequence, crystal structure determination and refinement of two crystal forms of lipase B from *Candida antarctica*," *Structure*, vol. 2, no. 4, pp. 293–308, 1994.
- [30] B. S. Lane and K. Burgess, "Metal-catalyzed epoxidations of alkenes with hydrogen peroxide," *Chemical Reviews*, vol. 103, no. 7, pp. 2457–2474, 2003.
- [31] M. G. Clerici, G. Bellussi, and U. Romano, "Synthesis of propylene oxide from propylene and hydrogen peroxide catalyzed by titanium silicalite," *Journal of Catalysis*, vol. 129, no. 1, pp. 159–167, 1991.
- [32] Y. Wang, Q. Zhang, T. Shishido, and K. Takehira, "Characterizations of iron-containing MCM-41 and its catalytic properties in epoxidation of styrene with hydrogen peroxide," *Journal of Catalysis*, vol. 209, no. 1, pp. 186–196, 2002.
- [33] K. Yamaguchi, K. Ebitani, and K. Kaneda, "Hydrotalcite-catalyzed epoxidation of olefins using hydrogen peroxide and amide compounds," *The Journal of Organic Chemistry*, vol. 64, no. 8, pp. 2966–2968, 1999.
- [34] S. Ueno, K. Yamaguchi, K. Yoshida, K. Ebitani, and K. Kaneda, "Hydrotalcite catalysis: heterogeneous epoxidation of olefins using hydrogen peroxide in the presence of nitriles," *Chemical Communications*, no. 3, pp. 295–296, 1998.
- [35] H. Munakata, Y. Oumi, and A. Miyamoto, "A DFT study on peroxy-complex in titanasilicate catalyst: hydrogen peroxide activation on titanasilicalite-1 catalyst and reaction mechanisms for catalytic olefin epoxidation and for hydroxylamine

- formation from ammonia," *The Journal of Physical Chemistry. B*, vol. 105, no. 17, pp. 3493–3501, 2001.
- [36] P. Wu and T. Tatsumi, "Extremely high trans selectivity of Ti-MWW in epoxidation of alkenes with hydrogen peroxide," *Chemical Communications*, vol. 10, no. 10, pp. 897–898, 2001.
- [37] W. T. Reichle, S. Y. Kang, and D. S. Everhardt, "The nature of the thermal decomposition of a catalytically active anionic clay mineral," *Journal of Catalysis*, vol. 101, no. 2, pp. 352–359, 1986.
- [38] D. Mandelli, M. C. A. van Vliet, R. A. Sheldon, and U. Schuchardt, "Alumina-catalyzed alkene epoxidation with hydrogen peroxide," *Applied Catalysis A: General*, vol. 219, no. 1–2, pp. 209–213, 2001.
- [39] R. G. Cesquini, J. M. de Souza e Silva, C. B. Woitiski, D. Mandelli, R. Rinaldi, and U. Schuchardt, "Alumina-catalyzed epoxidation with hydrogen peroxide: recycling experiments and activity of sol-gel alumina," *Advanced Synthesis & Catalysis*, vol. 344, pp. 911–914, 8, 2002.
- [40] M. S. Ashraf, B. A. Mansor, I. Nor Azowa et al., "Molecules synthesis of radiation curable palm oil-based epoxy acrylate: NMR and FTIR spectroscopic investigations," *Molecules*, vol. 20, pp. 14191–14211, 2015.
- [41] P. P. Kosheela Devi, A. H. Hazimah, T. I. Tuan Noor Maznee et al., "Optimisation on synthesis of acrylated epoxidised palm olein using response surface methodology," *Journal of Oil Palm Research*, vol. 27, pp. 366–376, 2015.
- [42] Malaysian Palm Oil Council (MPOC), "The oil palm tree," 2021, <http://mpoc.org.my/the-oil-palm-tree/>.
- [43] M. D. Khairul Zaman, *UV Overprint Varnish (OPV): Application of Epoxidized Palm Oil Acrylate (EPOLA)*, Proc. RadTech Asia, 2011.
- [44] I. H. S. Markit, "Specialty chemicals update program: radiation curable coatings," 2018, <https://www.ihs.com/products/chemical-radiation-curable-coatings-scup.html>.
- [45] D. Behera and A. K. Banthia, "Synthesis, characterization, and kinetics study of thermal decomposition of epoxidized soybean oil acrylate," *Journal of Applied Polymer Science*, vol. 109, no. 4, pp. 2583–2590, 2008.
- [46] P. Saithai, J. Lecomte, E. Dubreucq, and V. Tanrattanakul, "Effects of different epoxidation methods of soybean oil on the characteristics of acrylated epoxidized soybean oil-copoly(methyl methacrylate) copolymer," *Express Polymer Letters*, vol. 7, no. 11, pp. 910–924, 2013.
- [47] M. S. Ibrahim, N. G. Kandile, M. S. Hossam, and I. M. Moussa, *Development of Radiation Curable Surface Coating Based on Soybean Oil, Part I: Preparation and Characterization of Acrylated Oil*, Polym. Sci. Technol, 2005.
- [48] M. Rohani, R. Abdul Razak, A. M. Rohah, and M. Siti Noor Hidayah, "Mechanical, thermal and water absorption properties of epoxy/acrylated epoxidized palm oil/montmorillonite nanocomposite," *AIP Conference Proceedings*, vol. 2030, 2018no. 1, 2018.
- [49] R. Tajau, R. Rohani, and S. Mek Zah, "Physicochemical and thermal properties of acrylated palm olein as a promising biopolymer," *Journal of Polymers and the Environment*, vol. 28, no. 10, pp. 2734–2748, 2020.
- [50] M. Nurul Huda, N. S. Nik Ghazali, S. Mek Zah et al., *Development of UV Curable Overprint Varnishes (OPV) Formulation from Epoxidized Palm Olein Acrylated (EPOLA)*, Malaysia, 2014R&D Seminar, 2014.
- [51] N. R. Paluvai, S. Mohanty, and S. K. Nayak, "Synthesis and characterization of acrylated epoxidized castor oil nanocomposites," *International Journal of Polymer Analysis and Characterization*, vol. 20, no. 4, pp. 298–306, 2015.
- [52] G. S. Sudha, H. Kalita, S. Mohanty, and S. K. Nayak, "Castor oil modified by epoxidation, transesterification, and acrylation processes: spectroscopic characteristics," *International Journal of Polymer Analysis and Characterization*, vol. 22, no. 6, pp. 519–525, 2017.
- [53] A. Rana and R. Evitts, "Synthesis and characterization of acrylated epoxidized flaxseed oil for biopolymeric applications," *International Polymer Processing*, vol. 30, no. 3, pp. 331–336, 2015.
- [54] G. Wuzella, A. R. Mahendran, U. Müller, A. Kandelbauer, and A. Teischinger, "Photocrosslinking of an acrylated epoxidized linseed oil: kinetics and its application for optimized wood coatings," *Journal of Polymers and the Environment*, vol. 20, no. 4, pp. 1063–1074, 2012.
- [55] J. L. Wong, M. M. Aung, H. N. Lim, and S. N. A. Md Jamil, "Spectroscopic analysis of Epoxidised Jatropha Oil (ejo) and Acrylated Epoxidised Jatropha Oil (AEJO)," *Pertanika Journal of Tropical Agricultural Science*, vol. 40, pp. 435–448, 2017.
- [56] R. Wang and T. Schuman, "Vegetable oil-derived epoxy monomers and polymer blends: a comparative study with review," *Express Polymer Letters*, vol. 7, no. 3, pp. 272–292, 2013.
- [57] A. M. Díez-Pascual and A. L. Díez-Vicente, "Wound healing bionanocomposites based on castor oil polymeric films reinforced with chitosan-modified ZnO nanoparticles," *Biomacromolecules*, vol. 16, no. 9, pp. 2631–2644, 2015.
- [58] A. Barkane, O. Platnieks, M. Jurinovs, and S. Gaidukovs, "Thermal stability of UV-cured vegetable oil epoxidized acrylate-based polymer system for 3D printing application," *Polymer Degradation and Stability*, vol. 181, article 109347, 2020.
- [59] Y. Hu, P. Jia, Q. Shang et al., "Synthesis and application of UV-curable phosphorus-containing acrylated epoxidized soybean oil-based resins," *Journal of Bioresources and Bioproducts*, vol. 3, pp. 183–191, 2019.
- [60] W. Liu, M. Fei, Y. Ban, A. Jia, R. Qiu, and J. Qiu, "Concurrent improvements in crosslinking degree and interfacial adhesion of hemp fibers reinforced acrylated epoxidized soybean oil composites," *Composites Science and Technology*, vol. 160, pp. 60–68, 2018.