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Bio-resins are bio-based materials derived from vegetable resources, especially from vegetable seed oils. It is widely known that bio-resources are renewable, highly available, and sustainable. Resins and most polymers are largely derived from petroleum-based sources that are known to pose chemical risks. Resins have practical applications in printing inks, plasticisers and diluents, as well as in coating materials. Vegetable oils possess a large number of oxirane groups, which are essential for epoxidation to occur, resulting in the production of bio-resins. This undeniably serves as a promising candidate for competing with fossil-fuel-derived petroleum-based products. Thus, the aim of this review paper is to highlight aspects related to the production of bio-resins, including the chemical route of vegetable oil epoxidation process and its influencing factors, the reaction kinetics, bio-resins and the physico-chemical and mechanical properties of bio-resins, along with their applications. The resins industry has seen some remarkable progress towards the commercialisation of several bio-resins originating from vegetable oils, such as soybean oil, castor oil, and linseed oil. This success has undoubtedly intensified further efforts in fields related to bio-resin applications. Research and development is ongoing with the aim of customising a feasible formulation for the synthesis of bio-resins with the desired properties for catering to various applications

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Abstract: Bio-resins are bio-based materials derived from vegetable resources, especially from vegetable seed oils. It is widely known that bio-resources are renewable, highly available, and sustainable. Resins and most polymers are largely derived from petroleum-based sources that are known to pose chemical risks. Resins have practical applications in printing inks, plasticisers and diluents, as well as in coating materials. Vegetable oils possess a large number of oxirane groups, which are essential for epoxidation to occur, resulting in the production of bio-resins. This undeniably serves as a promising candidate for competing with fossil-fuel-derived petroleum-based products. Thus, the aim of this review paper is to highlight aspects related to the production of bio-resins, including the chemical route of vegetable oil epoxidation process and its influencing factors, the reaction kinetics, bio-resins and the physico-chemical and mechanical properties of bio-resins, along with their applications. The resins industry has seen some remarkable progress towards the commercialisation of several bio-resins originating from vegetable oils, such as soybean oil, castor oil, and linseed oil. This success has undoubtedly intensified further efforts in fields related to bio-resin applications. Research and development is ongoing with the aim of customising a feasible formulation for the synthesis of bio-resins with the desired properties for catering to various applications

Keywords: bio-resins; vegetable oil; epoxy; epoxidation; bio-products; bio-fuel

1. Introduction to Bio-Resins

A bio-based material is defined as a material that comes from organic materials containing carbon derived from renewable resources through a biological process, which commonly includes all plants and animal mass. Thus, bio-resins are resins that are derived from biological sources such as vegetable oils instead of petrochemicals. A bio-resin is a polymer or plastic made from new carbon resources, which is obtained from renewable and sustainable agricultural crops, as well as residual agricultural waste. Corn, sugar and forest resources [1] are examples of agricultural crops, whereas rice straw, grapevine trimmings, corn husks and sugarcane bagasse are examples of agricultural waste.

There are two major renewable resources available in large quantities on Earth: cellulose and vegetable oils. Vegetable oils are the most preferred in industry, because they are widely used in the

preparation of polymeric binders for coating formulations, flooring materials and resin applications, in comparison to cellulose, which lacks applications in the field of polymeric coatings [2].

Vegetable Oils as a Dominant Source of Epoxy Bio-Resins

Vegetable oils are composed of fats and lipids, which are comprised of triglyceride molecules. They contain a large amount of unsaturated fatty acids that can be converted into epoxy fatty acid. The predominant molecules in vegetable oils are triglyceride molecules, which are also known as triacylglycerols (TAGs). They consist of three chains of fatty acids attached together with glycerols. Epoxidised vegetable oil has been widely used as the starting material for the synthesis of various chemicals, such as polyols, glycol, carbonyl compounds and lubricants, as well as plasticisers [3]. Vegetable oils have been widely used in various applications as raw materials because of their availability, low cost and bio-degradability [4].

Vegetable oils have more advantages rather than disadvantages. The best properties of vegetable oils in terms of their usage as base oils for lubricants are their high viscosity index, high flash point, high lubricity, low loss through evaporation, high bio-degradability, low volatility owing to the high molecular weight of the TAG and low toxicity [5,6]. Meanwhile, vegetable oils are well known for possessing low thermal, oxidative and hydrolytic stability, along with low-temperature characteristics that are typically due to the presence of unsaturated carbon double-bond fatty acids [5]. All of these properties of vegetable oils are as a result of their fatty acid composition. The best compositions of unsaturated fatty acids for use in the production of epoxides are oleic, linoleic and linolenic acyl groups [7]. These oleochemicals can easily be found, for example, in linseed oil, rapeseed oil, olive oil, corn oil and sunflower oil.

Vegetable oils require low-cost processing, are easily bio-degradable and are readily available [8], permitting them to compete with petroleum-based products. The most outstanding characteristic of vegetable oils is their unique structure, which reacts to unsaturated sites, epoxies, hydroxyls, esters and many more functional groups [9]. Vegetable oils with these functional groups would pass on inherent fluid characteristics to the product of the reaction. Consequently, the transformation of a vegetable oil after it undergoes various chemical reactions enables the production of low-molecular-weight polymers for numerous applications, including the preparation of inks, diluents, plasticisers, lubricants, agrochemicals, food and composite materials [10–12].

Hence, vegetable oils have been reported to be the best alternative candidates for the production of bio-resins, especially in the thermosetting of industrial resins, as they can be polymerised. Thermosetting resins are the most needed material in many industries, such as construction, furniture and the automotive industry. Introducing this bio-based material would help replace glass fibres, which are currently synthesised from petrochemical materials. As a result, the industry would turn into a greener, healthier, and safer sector.

2. Epoxidation

2.1. Principles

Epoxidation of vegetable oils is defined as a process of adding a single atom of oxygen to each unsaturated fatty acid chain (C=C) using oxidising agents, which would change the original unsaturated fatty acid chain into an epoxy group. The oxidising agents that could be utilised are percarboxylic acids, inorganic peroxides and organic peroxides. The conversion efficiency of chains could be monitored directly and indirectly via the oxirane oxygen content (OOC) and iodine value, respectively [7].

Epoxidation has been applied under different conditions by previous researchers, depending on the feedstock, epoxidation reagent, catalyst and solvent. Epoxidation of vegetable oils can be performed in solution or in bulk, which also has two choices, either in situ peroxyacid or ex situ peroxyacid. Hence, the process has an option of using either heterogeneous catalysts or homogenous

catalysts. However, in situ peroxyacid formation has been reported to be the most favourable process owing to the safety issue in which concentrated peroxyacid is truly unstable and explosive [13].

Epoxy resins have been synthesised from many renewable resources, especially vegetable oils. There are two ways of producing epoxy polymers: epoxidation of double bonds in vegetable oils with active oxygen and also glycidylation of the hydroxyl group present in the vegetable oils with epichlorohydrin. For example, epoxy monomers from linseed oil or palm oil are synthesised through epoxidation, whereas epoxy monomers from castor oil are synthesised through glycidylation [14].

2.2. Epoxidation Method

Epoxidation methods can be categorised into four types: conventional epoxidation (also known as Prilezhaev epoxidation), acidic ion exchange resin (AIER) epoxidation, chemo-enzymatic epoxidation and metal-catalysed epoxidation [3,4]. Table 1 presents the descriptions of these types of epoxidation, which were commonly used by previous researchers.

The first epoxidation process is called Prilezhaev epoxidation. This process (conventional process) involves in situ epoxidation with highly strong mineral acids, such as hydrochloric acid, nitric acid, sulfuric acid and phosphoric acid, which act as the catalyst for the reactions [4]. However, this process lacks selectivity for epoxides owing to the presence of a homogeneous catalyst in the mixture, causing a problem in the separation of the final products from the acidic by-products [15].

The second method of epoxidation is chemo-enzymatic epoxidation. In this process, an enzyme such as immobilised *Candida antarctica* Lipase B is used in the reaction as a catalyst [7]. However, Saurabh [15] reported that this enzyme is not suitable for the epoxidation process because of its low stability at high temperatures and high concentration of hydrogen peroxide.

Metal-catalysed epoxidation is another method of epoxidation [15]. This method utilizes the transition of a metal catalyst in the process of epoxidation, such as silver, titanium, tungsten, rhenium, molybdenum and nitrile. Among these, nitrile is the most commonly used catalyst in epoxidation. However, it was reported that epoxidation using an inorganic catalyst is not environmental friendly owing to the involvement of hypohalous acids (HOX) and salts. Furthermore, Manthey [16] stated that using silver metal as a catalyst in the epoxidation process is also unsuitable because it only works with simple ethylenic substrates.

The last technique of epoxidation is called the AIER method [15]. In this method, an AIER is used as a catalyst during the epoxidation reaction. In comparison, this technique was found to be the most efficient and environmental friendly [15,16]. The fact that AIERs are heterogeneous catalysts has made the purification of epoxides easier with a high-selectivity epoxidation reaction. Consequently, this helps in suppressing side reactions. Many researchers attempted to describe the mechanism of the *in situ* epoxidation of vegetable oils with peroxyacetic acid or peroxyformic acid in the presence of a catalyst. Most of the researchers used homogenous catalysts in their epoxidation processes, namely, an SO_3H–functional Brønsted acidic ionic liquid [17], sulphuric acid [18,19], phosphoric acid, nitric acid and hydrochloric acid [20]. Generally, the mechanism for in situ epoxidation in the presence of a catalyst involves multiple steps [17,21,22], as depicted in Table 1. Initially, peroxyacetic acid is formed in the aqueous phase in the presence of a catalyst, followed by the reaction of the peroxyacetic acid with the double bond of ethylenic unsaturation in the organic phase. Simultaneously, degradation of the oxirane ring occurs, producing many side products, namely, diol, hydroxyl ester, hydroxyl carboxylic acid and hydroxyl acetate (the most favourable) [20,23].

Table 1. Types of Epoxidation Methods.

No	Types of Epoxidation Method	Description	Ref
1	Conventional epoxidation process/Prileshajev-epoxidation process	Special requirement of chemicals: Epoxidation using strong mineral acid such as HCl, HNO$_3$, H$_2$SO$_4$, H$_3$PO$_4$ (acts as a homogeneous catalyst)	[4]
		Reaction: Step 1: $vegetable\ oil \xrightarrow{strong\ acids} performic/peracetic\ acid$ Step 2: transfer of acids to organics phase Step 3: Epoxidation $\quad peracetic\ acid \xrightarrow{organic\ phase} formic\ acid + epoxy$	[4]
		Side Reactions: Oxirane ring opens to diols, hydroxyl esters, estelloids, and other dimer formation. Diadvantages Undesirable side reactions, expensive purification and hence causes epoxides to be less attractive as a starting material for any industry	[3]
2	Ion exchange resin (AIER) epoxidation	Special requirement of chemicals: Epoxidation process using AEIR as an insoluble gel catalyst which is an organic polymer bead with small yellowish physical appearance. Reaction: Step 1: $vegetable\ oil + hydrogen\ peroxide \rightarrow peroxy\ acid$ Step 2: Epoxidation $\quad peroxy\ acid \xrightarrow{AEIR\ solid\ catalyst} epoxides$	[3,4]
		Side Reactions: Oxirane ring opens to oxirane rings opens to diol, hydroxy ester, hydroxyl carboxylic n hydroxyl acetate Advantages Avoid the use of strong acids, suppress side reactions, easy and simple in the separation of acid from epoxides, low degradation of oxirane ring, environmental friendly and able to make the epoxidation process cleaner	[3,4]
3	Chemo-enzymatic epoxidation	Special requirement of chemicals: Epoxidation process using immobilized *Candida antartica Lipase B* as the catalyst. Reaction: Step 1: $vegetable\ oil + hydrogen\ peroxide \rightarrow peroxy\ acid$ Step 2: Self-Epoxidation $\quad peroxy\ acid \xrightarrow{enzyme\ catalyst} epoxides$	[7]
		Advantages Avoid the use of strong acids, suppress side reactions, easy and simple in the separation of acid from epoxides, low degradation of oxirane ring, environmental friend and able to make the epoxidation process cleaner	[4,24]
4	Metal-catalyzed epoxidation	Special requirement of chemicals: Epoxidation using high-valence catalysts such as molybdenum, titanium, tungsten or rhenium. Reaction: Step 1: $vegetable\ oil + hydrogen\ peroxide \rightarrow peroxy\ acid$ Step 2: Self-Epoxidation $\quad peroxy\ acid \xrightarrow{high\ valences\ catalyst} epoxides$	[25]
		Advantages Requires only a few amounts of H$_2$O$_2$ and shorter the reaction times, avoid the use of strong acids, suppress side reactions, easy and simple in the separation of acid from epoxides, low degradation of oxirane ring, environmental friend and able to make the epoxidation process cleaner	

3. Factors Affecting Epoxidation

3.1. Mole Ratio of Hydrogen Peroxides to Ethylenic Unsaturation

One of the requirements for the epoxidation process to occur is the presence of an oxygen donor. The most common oxygen donor used in this process is hydrogen peroxide. Hydrogen peroxide is a good oxygen donor because it has low solubility in oils, which would be more beneficial to the final product of the process as it requires a small amount of energy for hydrogen peroxide removal from the final product [26]. Requiring a small amount of hydrogen peroxide in the epoxidation process is mainly preferred as it would result in a low-cost process [7]. Table 2 shows the mole ratios that have been used for epoxidation.

Table 2. Ratio of H_2O_2 to ethylene unsaturated carbon.

No.	Compound of Ethylenic Unsaturation	Optimum Ratio (H_2O_2/Ethylenic Unsaturation)	Ref.
1	Cottonseed oil	1.1–2.5 (1.1, 1.5, 2.0, 2.5)	[24]
2	Jatropha oil	0.8–2.5 (0.8, 1.1, 1.5, 2.5)	[13]
3	Jatropha oil	0.8–2.5 (0.8, 1.1, 1.5, 2.5)	[26]
4	Jatropha oil	2.5–4.5 (2.5, 3.0, 3.5, 4.0, 4.5)	[7]
5	Cottonseed oil	1.5–2.5 (1.5, 2.0, 2.5)	[24]
6	Fatty acid methyl ester (FAME)	0.8–2.5 (0.8, 1.1, 1.5, 2.5)	[17]

The mole ratio of hydrogen peroxide to ethylenic unsaturation has been chosen to be from 0.8 to 2.5 [13,25]. Studies have shown that the conversion of unsaturated ethylene to an oxirane ring increases with the increase in the concentration of hydrogen peroxide. However, a mole ratio of 2.5 was shown to be the highest ratio for maximum conversion to an oxirane ring with a very poor stability of the oxirane ring. This is because a high concentration of hydrogen peroxide accelerates the rate decomposition of oxirane rings in epoxies [25]. On the other hand, a low concentration of hydrogen peroxide has shown progressive conversion to an oxirane ring with a decrement of iodine value as well as an increment of oxirane value [13,24].

3.2. Mole Ratio of Organic Acids to Ethylenic Unsaturation

An organic acid is required in epoxidation to react with the hydrogen peroxide to form peroxyacid in the aqueous phase reaction. The peroxyacid is then transferred to the organic phase, which then reacts with the vegetable oil and directly produces epoxides. During this reaction, the unsaturation bond in the vegetable oils reacts with the peroxyacid, which then forms an oxirane ring in the molecule. Then, the organic acid is transferred back into the aqueous phase. It has been proven that the epoxidation reaction will not occur in the absence of peroxyacid [24].

Peroxyacid is formed when the organic acid, which acts as the oxygen carrier, reacts with the hydrogen peroxide, which acts as the oxygen donor. Several organic acids are used in epoxidation, such as acetic acid (CH_3COOH), formic acid (HCOOH) and benzoic acid [26,27]. The peroxyacid that forms during that reaction is in the aqueous phase. Several peroxyacids are available, such as peroxyacetic acid, peroxyformic acid, peroxybenzoic acid, peroxyfluoracetic acid, *m*-chloroperoxybenzoic acid and *m*-nitroperoxybenzoic acid [26].

There are two types of peroxyacids: preformed (ex situ) peroxyacid and in situ peroxyacid. In situ peroxyacid is usually preferred owing to the safety in its preparation and handling. Peroxyacids are unstable and explosive at high concentrations; thus, it is difficult prepare peroxyacids ex situ. Moreover, in situ peroxyacids only require a small amount of reactant, which is highly beneficial to the epoxidation process [26].

Organic acids participate in two ways during the epoxidation reaction: as a catalyst for oxirane ring formation and as a reactant in the hydrolysis of the oxirane ring [26]. Therefore, the level of

organic acid used in the reaction must balance these two effects to ensure that the organic acid reacts at an optimum level and results in the maximum OOC.

Table 3 shows the ratio of acetic acid to double bonds in the epoxidation reaction. The mole ratio of organic acid to ethylenic unsaturation was varied from 0.25 to 1 per mole of ethylenic unsaturation to investigate its effect on the kinetics of the epoxidation process [13,26]. The mole ratio ranges of organic acids to ethylenic unsaturation, which were obtained by previous researchers, are 0.25:1, 0.3:1, 0.5:1, 0.65:1, 0.75:1 and 1:1. Based on Sinadinović-Fišer [24] oxirane conversion was initially relatively high in the presence of formic acid compared to acetic acid. However, as time progressed, the final value of oxirane content increased gradually with the decrement of iodine value for the case of acetic acid, whereas oxirane conversion increased until a maximum value and then decreased with time. This means that acetic acid performed best with a small amount of undesired product at the end of the reaction, although the rate of oxirane ring formation was slow.

Table 3. Ratio of acetic acid to ethylene unsaturated carbon.

No.	Compound of Ethylenic Unsaturation	Optimum Ratio (CH_3COOH/Ethylenic Unsaturation)	Ref.
1	Cottonseed oil	0.25–7.50 (0.25, 0.35, 0.50, 0.75)	[24]
2	Jatropha oil	0.3–1.0 (0.30, 0.50, 0.65, 1.00)	[13]
3	Jatropha oil	0.3–1.0 (0.30, 0.50, 0.65, 1.00)	[26]
4	Cottonseed oil	0.3–0.5 (0.3, 0.4, 0.5)	[19]
5	FAME	0.3–0.9 (0.3, 0.5, 0.7, 0.9)	[17]

3.3. Reaction Temperature

The temperature of the mixture has been reported to be one of the variables that affect the epoxidation process. A high temperature in the epoxidation process has been shown to be detrimental to the process as it leads to ring opening, which would decrease epoxy production in the final product [26,27]. It has also been reported that, with the increase in temperature, the rate of epoxidation also increases until a maximum value is attained. Between 30 °C and 45 °C, conversion to oxirane relatively increases within the experimental time limit [24]. Meanwhile, at the maximum temperature (more than 60 °C), the OOC value initially increases and then gradually decreases. At 75 °C, the percentage conversion to oxirane relatively decreases after some increment at the initial phase of the epoxidation reaction [24]. From this, it can be concluded that increasing the temperature of the reaction tends to increase the epoxidation rate as well as the rate of hydrolysis (oxirane cleavage) of the product. On the other hand, decreasing the temperature of the reaction leads to a low epoxidation rate with high product stability as a result of less ring opening.

The epoxidation rate of jatropha oil by in situ peroxyacetic acids has also been assessed at various temperatures, ranging from 30 °C to 85 °C [7,13], as shown in Table 4. A reaction temperature below 70 °C is considered the best temperature for the formation of peroxyformic acid, whereas a higher temperature (85 °C) is suitable for peroxyacetic acid [26]. The optimum temperature for epoxidation of cottonseed oil was found to be 60 °C [19,24].

Table 4. Temperature of epoxidation.

No.	Compound of Ethylenic Unsaturation	Temperature of the Reaction (°C)	Ref.
1	Cottonseed oil	30–75 (30, 45, 60, 75)	[24]
2	Jatropha oil	30–85 (30, 50, 70, 85)	[13]
3	Jatropha oil	30–85 (30, 50, 70, 85)	[26]
4	Jatropha oil	40–70 (40, 45, 50, 60, 70)	[7]
5	Cottonseed oil	50–60 (50, 55, 60)	[19]
6	FAME	30–85 (30, 50, 70, 80)	[17]

3.4. Stirring Speed

Table 5 illustrates the ranges of the stirring speeds for epoxidation that have been adopted by previous researchers. The most favourable stirring speed for epoxidation, in which the reaction is not substantially affected by this parameter, is beyond 1500 rpm. Previous researchers have reported that, for most of the reactions, the mixture is free from mass transfer resistance at a speed greater than 1500 rpm [25]. Work has previously been conducted on the epoxidation of jatropha oil with toluene at a speed of 2500 rpm to ensure that the reaction is kinetically controlled and homogeneously mixed [25].

Table 5. Stirring speed of epoxidation.

No.	Compound of Ethylenic Unsaturation	Stirring Speed (rpm)	Ref.
1	Jatropha oil	Ratio: 500–2500 Optimum: 1500 Carried out: 2500	[13]
2	Cottonseed oil	Ratio: 600–2400 Optimum: 1800 Carried out: 2400 ± 25	[24]
3	Jatropha oil	Ratio: 1000, 1500, 2000, 2500 Optimum: 1500	[26]
4	Cottonseed oil	Ratio: 300–1200	[19]

3.5. Spectroscopic and Titration Analysis of Epoxy Bio-Resin

The epoxy structure of the epoxidation of fatty acids in vegetable oils can be determined through the concentration of double bonds in the product by performing several analyses as discussed below.

3.5.1. Iodine Value Analytical Analysis

The physico-chemical properties of vegetable oils and epoxides were calculated on the basis of the ASTM and American Oil Chemists' Society (AOCS) standard official methods [9,28]. The typically measured properties were the acid value, density, iodine value, kinematic viscosity, pour point, specific gravity and oxirane oxygen content (OOC) on the basis of the methods of AOCS (Te la-54, 1997), ASTM D 4052-91, AOCS (Tg 1-64, 1997), ASTM D-445, ASTM D-97, ASTM D854-10 and AOCS Cd 9–57, respectively [6]. The main chemical properties that are crucial for the epoxidation reaction are the iodine value and OOC. The iodine value is important in determining the tendency of the vegetable oil to produce epoxides through epoxidation.

A relatively high iodine value in vegetable oils reflects a high content of unsaturated fatty acids [4]. This is favourable for epoxidation as it would encourage high production of epoxides. A high content of linoleic acid and oleic acid is known to be a good source of unsaturated fatty acids (lauric acid), which is required for promoting a successful epoxidation process [29]. Once the epoxidation process takes place, the iodine value of the oil decreases. Table 6 summarises the iodine values of several types of vegetable oils.

Table 6. List of iodine values for several vegetable oils.

No.	Oil	Iodine Value (g/100 g)	Ref.
1	Crude palm oil	53	[30]
2	Jatropha oil	105.68	[31,32]
3	Kenaf oil	86.3	[29]
4	Peanut oil	123.22	[33]
5	Coconut oil	9.9	[34]
6	Rapeseed	97–108	[3]
7	Corn oil	127–133	[3]
8	Sunflower oil	118–141	[3]
9	Rubber seed oil	136.2	[35]

3.5.2. OOC Analytical Analysis

The concentration of epoxide produced can be determined on the basis of the concentration of oxirane (OOC) in the product of epoxidation of vegetable oils using the standard official method of AOCS Cd 9-57. A formula is used to identify the concentration of the epoxy in the product. The theoretical value of the oxirane content and the relative percentage conversion to oxirane can be calculated using the following equations:

$$OO_{\text{theoretical}}, \% = \left[\frac{\left(\frac{IV_o}{2A_i} \right)}{100 + \left(\frac{IV_o}{2A_i} \right) A_o} \right] \times A_o \times 100 \tag{1}$$

where

A_i = atomic weight of iodine (126.9);
A_o = atomic weight of oxygen (16)
IV_o = initial iodine value of oil sample

$$\text{Relative percentage conversion to oxirane}, \% = \left[\frac{OO_{\text{exp}}}{OO_{\text{the}}} \right] \times 100 \tag{2}$$

where;

OO_{exp} = experimentally oxirane oxygen content measured based on the standard official method
OO_{the} = theoretically oxirane oxygen content in 100 g of epoxides.

3.5.3. Fourier Transform Infrared Spectroscopic Analysis

The purpose of Fourier transforms infrared (FTIR) spectroscopy is to identify the functional group present in the sample [36]. In this study, the main purpose of the FTIR test was to detect the presence of an oxirane ring in the product after going through epoxidation [24]. A list of epoxy peaks for different vegetable oils is shown in Table 7. FTIR spectra were recorded in transmission mode between 4000 and 500 cm^{-1} with a nominal resolution of 4 cm^{-1} [37]. An oxirane ring can be detected within the ranges 750–880 cm^{-1} and 815–950 cm^{-1} [7].

Table 7. FTIR results of the epoxy existence in the compound.

Raw Material	Stretching Vibration Peak Double Bond or C=C Bending Vibration Peak of Aliphatic Carbon (cm^{-1})	Peak for Epoxy Group, C–O, or Epoxy Ring (cm^{-1})	Ref.
Cottonseed oil	3010	823, 843	[19]
Palm olein from palm oil	3003	844	[7]
Jatropha oil	3012	826, 842	[37]
Linoleic acid	3009	820	[24]
Castor oil	3400	820–843	[6]
Rubber seed oil	3009	824	[38]

3.5.4. ^{1}H NMR Spectroscopic Analysis

NMR is an analytical chemical technique used to identify the molecular structures present in an organic compound, allowing the investigation of the properties of that compound. ^{1}H NMR mainly focuses on the detection of the proton number in a molecule or sample as well as how each proton interacts (couples) with other protons. ^{1}H NMR is the most valuable characterisation method in lipid analysis, especially in this research, which involves the utilisation of vegetable oils, as shown in Table 8. The frequency with which protons at any hydrogen atom in an organic compound resonate strongly depends on the molecular environment.

Table 8. ^{1}H NMR results in an epoxy compound.

No.	Oil	Signal of Epoxides [–CH–O–CH–] (ppm)	Ref.
1	Linoleic acid	2.92–3.12	[24]
2	Castor oil FAME	2.9–3.2	[6]
3	Hemp oil	2.8–3.3	[1]

3.5.5. ^{13}C NMR Spectroscopic Analysis

^{13}C NMR spectroscopy mainly focuses on the detection of carbon activity in the sample, shown as a peak in the spectrum. The main purpose of using ^{13}C NMR spectroscopy in this research was to identify the presence of an epoxy ring group in the epoxides. ^{13}C NMR is considered to be one of the reliable molecular structure characterisation methods owing to its distinctive signals for all carbon atoms in organic compounds [24]. The spectrum of the epoxy ring in monoepoxide linoleic acid is within the range of 54.59–57.29 ppm [24]. Table 9 summarises the peak carbon activity present in the product of epoxidation.

Table 9. ^{13}C NMR results in an epoxy compound.

Raw Material	Carbon Chemical Shift (ppm)		Ref.
	Unsaturated Carbon (C=C)/Olefinic Carbon	C–O	
Palm olein from palm oil	100–150	40–80	[7]
Linoleic acid	128.27–130.38	54.59–57.29	[24]
Rubber seed oil	100–150	53–60	[38]

4. Kinetics of Epoxidation

Different types of epoxidation have different types of kinetics, depending on the type of catalyst used in the epoxidation reaction [25]. The catalyst in this case does not participate in the reactions. Both homogenous and heterogeneous models are commonly used in epoxidation, although the kinetics of the heterogeneous approach are more complex compared to the homogenous one, as presented in Table 10.
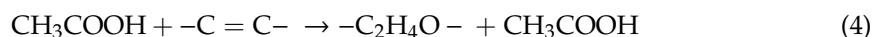
Table 10. Kinetics of epoxidation.

Type of Epoxidation	Kinetic Model Approach	Ref.
Conventional epoxidation	Homogeneous model approach	[18,19,24,26]
Ion exchange resin	Homogeneous and heterogeneous approaches	[13,21,39,40]
Chemo-enzymatic epoxidation	Heterogeneous approach	[25]
Metal-catalysed epoxidation	Homogeneous and heterogeneous approaches	[41]

The mechanism of the homogenous approach can be generalised into three reactions with three major assumptions: (i) the reaction of the in situ peroxyacid formation is considered to be the rate-determining step, (ii) the concentration of peroxyacid is constant throughout the reaction and (iii) the reaction is a pseudo-first-order one [18,24,26,28]. Details of the reactions are as follows.

i.   In Situ peroxyacid formation:

$$CH_3COOH + H_2O_2 \overset{H^+}{\Leftrightarrow} CH_3COOH + H_2O \tag{3}$$

ii.   The reaction of peroxyacid with double bond of oil:

$$CH_3COOH + -C = C- \rightarrow -C_2H_4O- + CH_3COOH \tag{4}$$

iii. The reaction of the oxirane ring with acetic acid leads to the formation of hydroxyl acetate by-product:

$$-C_2H_4O- + CH_3COOH \rightarrow -CH(OH) - CH(OCOCH_3)- \tag{5}$$

$$\text{Overall reaction}: \ln[(H_2O_2) - (\%\text{oxirane})] = -k(RCOOH)_0 t + \ln(H_2O_2)_0 \tag{6}$$

where, $(H_2O_2)_0$ is the initial concentration of hydrogen peroxide, $(RCOOH)_0$ is the initial concentration of formic acid, t is the reaction time, and k is the rate constant.

Thus, from the overall reactions, a plot of $\ln[(H_2O_2) - (\%\text{oxirane})]$ versus time is expected to yield a straight line with a slope of k(RCOOH). Subsequently, the value of k can be determined from the slope and should be different for each temperature. As with a typical chemical reaction, the epoxidation reaction rate (k) increases as the temperature increases.

Generally, the value of the activation energy (E_a) can be obtained from the Arrhenius relationship.

$$\ln k = \ln A - \frac{E_a}{RT} \tag{7}$$

in which;

k: Reaction rate

A: pre-exponential factor which can be determined from the y-intercept

Ea: activation energy which can be determined from the slope

R: universal gas constant ($8.314 \text{ J·mol}^{-1}\text{·K}^{-1}$)

T: temperature of the experiment

Meanwhile, the kinetics and mechanism for the epoxidation of vegetable oils by ion exchange resins have been considered using two different models: a pseudo-homogenous model and a heterogeneous model. The pseudo-homogenous model assumes that the reactions depend on two phases (oil/water), whereas the heterogeneous model assumes that the reactions occur in three phases (oil/water/ion exchange resin) [24]. The pseudo-homogenous approach has been applied as the kinetic model for the epoxidation of vegetable oils using an ion exchange resin by assuming the presence of a resin solely as the source of protons, and it does not involve the reaction of epoxidation [21].

Sinadinović-Fišer [22] performed a kinetics study on the epoxidation of castor oil with the *in situ* formation of peroxyacetic acid in the presence of ion exchange resins. In that study, it was assumed that the reaction occurred in a homogeneous fashion as the stirring of the mixture was exceptionally good that the diffusional resistance in the reaction mixture could be considered negligible. This led to a second assumption that the acidic ion exchange was uniformly distributed during epoxidation and complete dissociation of sulphur groups was achieved in the liquid phase. The ion exchange resin that dissolves in the mixture was assumed to most likely behave similarly to a homogeneous catalyst. As a consequence, no catalyst was considered in the kinetics study. Applying the pseudo-homogeneous model, these researchers concluded that the reaction in Equation (3) is the rate-determining step in the pseudo-first-order reaction [22].

On the other hand, the heterogenous model approach assumes that the reactions proceed in three stages [13]: (1) adsorption of at least one of the reactants on the active site of the catalyst,

(2) chemical reaction between the surface of the adsorbed molecules and the surface of the adsorbed and un-adsorbed molecules and (3) desorption of the products. Goud [13] described the epoxidation mechanism of jatropha oil with peroxyacetic acid and peroxyformic acid in the presence of an ion exchange resin by applying the model of Langmuir–Hinshelwood–Hougen–Watson, which took into account the catalyst into the reaction kinetics. The model showed that three steps occurred with the active catalyst: (i) adsorption of at least one of the reactants on the catalyst surface, (ii) surface reaction between molecules (adsorbed/adsorbed or adsorbed/un-adsorbed) and (iii) desorption of the products. It was assumed as well that there is no resistance to mass transfer at any interface (solid/liquid and liquid/liquid) owing to the good stirring of the mixture. Therefore, the diffusional resistance and steps of transport phenomena in the reaction kinetics were neglected. Reaction (1) is considered to be the rate-limiting step and to be heterogeneous as the concentration of the catalyst was included in the rate law.

5. Physical, Mechanical and Chemical Characterisation of Epoxy Bio-Resins

5.1. Physical Characterisation

Resins are cured before performing physical tests to assess scratch hardness (SH) [28], percentage of adhesion [28], glossiness [28], flexibility [28], impact resistance (IRt) [11] and thermal behaviour [29].

Glossiness is high in materials that have a high content of acrylic monomers. Meanwhile, the flexibility of a resin can be tested by performing the conical mandrel bend test to test the bending ability of the material. The characteristics of SH, adhesion and IRt mainly depend on the cross-linking in the resin and polarity of the structure. High-polarity resins exhibit good adhesion between the resins and substrates [11]. The solubility of bio-resins can also be assessed by mixing the resins in various polar and non-polar solvents in a closed test tube for a day. Then, the solubility of the mixture is determined through some tests based on standard laboratory methods, such as the hydroxyl value, specific gravity and refractive index [9]. Another physical test that can be performed on cured resins is to assess the number of drying cycles required for the resin to be surface-dried. It has also been reported that materials that have high molar mass and cross-linking require a short drying time [11].

5.2. Mechanical Characterisation

Tensile strength and flexural properties are two of the most important mechanical properties in resin mechanical characterisation. Tensile strength is tested by subjecting a sample to controlled tension until failure. Normally, the sample to be tested is cut into a specific size and undergoes curing before being tested. Regarding the tensile properties, a tensile machine is used in accordance with ASTM D638 to directly measure properties such as the ultimate tensile strength, breaking strength, maximum elongation and reduction in area (which can be analysed to determine the tensile strength), Young's modulus, stress, strain and Poisson's ratio [41].

On the other hand, flexural tests are used to determine the amount of force necessary to bend a beam of material, as well as its resistance to flexing or stiffness. These tests are conducted using appropriate machines in accordance with ASTM D7264 or ISO 178 to determine the flexural strength and modulus [41]. Three-point and four-point bending tests are available for assessing the flexural strength; the difference between them is that, in the latter, loading is experienced at two points simultaneously.

5.3. Chemical Characterisation

The chemical criteria that can be assessed for the epoxidation of oils are the peroxide value, iodine value, saponification value and free fatty acid content, using the official methods of the AOCS, namely, AOCS Cd 8b-90, AOCS Cd 1-25, AOCS Cd 3-25 and AOCS Ca 5a-40, respectively [29]. These characteristics are then analysed by performing a comparison between the oil (before epoxidation) and the epoxide (after epoxidation), which has already been performed by many researchers.

The chemical resistance of a resin to a specific type of reagent is another characteristic that can be analysed for epoxy resins by calculating the weight change of the cured resin after an appropriate amount is immersed in reagents for one month. The reagents used are hydrochloric acid (HCl), sodium hydroxide (NaOH), sodium chloride (NaCl) and distilled water. It has been reported that larger weight changes mean less resistance of resins to their respective reagents [28].

In addition, the thermal stability of resins can be tested using thermogravimetry (TG). Research has been performed on the analysis of epoxy soybean oil with TG analysis using a Netzsch STA 409 PC/PG analyser at a heating rate of 10 °C/min from 25°C to 700 °C under a N_2 atmosphere with a flow rate of 30 mL/min. The test required about 10 mg of sample for each test [38].

6. Synthetic Epoxy Resin versus Bio-Based Epoxy Resin

Current commercial synthetic epoxy resins are based on the diglycidyl ethers of bisphenol-A (BPA), bisphenol-F or other phenolic compounds. As chemicals, commercial resins are generally associated with various hazards (chemical, health, safety, environmental, etc.). The commercial synthetic epoxy resin DGEBA, for instance, is produced by the reaction of BPA (source of oxirane ring groups) with epichlorohydrin via a basic catalyst. The Food and Drug Administration has banned the use of BPA itself in synthesising baby bottles and food containers because of its potential hazards as an endocrine-disrupting chemical [42]. This caused serious concerns and, thus, prompted its continuous assessment and tight regulation. Furthermore, chemical-based resins derived from petroleum are being depleted and may not be viable in the long run.

Bio-based epoxy resins has been reported in many applications, including derivatives in the production of paintings and coatings, plasticisers, lubricant base stocks, reactive diluents, protection agents and surfactants [24]. This helps reduce the dependency on petrochemical-based feedstock and also has an acceptable, promising product performance with good service life [12,24]. Bio-based epoxy cross-linked polymers are one of the main versatile components in the production of thermosetting resins. They have also been used commercially in the applications of coatings, electrical/electronic laminates, adhesives, composites, flooring and paving [14]. Although bio-based epoxy polymers help reduce the consumption of non-renewable resources and the emission of greenhouses gasses, the non-existence of an aromatic ring in their structure has resulted in a low resistance of thermal and mechanical properties. Therefore, many studies have been performed to improve these shortcomings by introducing a binder such as cardanol to link the presence of aromatic structures to organic polymers. The presence of binder was found to be favourable in the epoxidation of phenolic compounds in condensed tannins [14].

Not only are bio-based epoxy resins renewable, natural resources, but also they are cheap, sustainable and bio-degradable and can be produced through facile synthesis methods. One of the most extensively available bio-based resins on the market is epoxidised soybean oil [43]. The market for this particular bio-based resin is projected to about 300 million USD in 2020. Intensive research has been performed to improve the properties of soybean resins in order to meet a wide range of applications [44]. Another successful bio-based resin is the epoxidised castor oil [45], which has been successfully commercialised to produce high-performance resins for wide-ranging markets, such as footwear, eyewear, cell phones and automotive parts. Linseed oil is also making its way to the market with more investigations underway to improve its formulation [43,46]. Several candidates of vegetable oils, such as canola oil, karanja oil and jatropha oil, have also demonstrated promising development to be commercialised. Efforts have also been made to mix petroleum-based products with bio-based ones in order to reduce the dependency on chemicals [47]. Although the commercialisation of bio-based resins is slow, it has successfully paved the way and more is anticipated in the near future.

7. Conclusions

Vegetable oils are widely used by researchers because of their large quantity and availability, as they can be extracted from various plant parts, such as seeds, kernels, fruits and shells. The constituents

of the vegetable oils, which commonly consist of multi-components of fatty acids and glycerol, enable the vegetable oils to produce resins by some chemical modification in the synthetisation process. AIER epoxidation is currently the most favourable method owing to its efficiency, ease and simplicity. Besides the availability of oxirane groups, temperature is the main determining factor that governs the success of epoxidation. Both homogeneous and heterogeneous kinetic models are compatible with the epoxidation process, depending on the nature of the catalyst. Developing a highly sophisticated technology with the ability to control this highly exothermic epoxidation reaction can offer further advancements in this field. The era of replacing petroleum-based polymers is currently gaining acceptance, with several successful commercial bio-based resins available now on the market. Currently, more research is performed to customise bio-resins with improved properties for serving various applications.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Manthey, N.W. Development of Hemp Oil Based on Bioresins for Biocomposites. Ph.D. Thesis, University of Southern Queensland, Toowoomba, Australia, 2013.
2. Chaudhari, A.; Gite, V.; Rajput, S.; Mahulikar, P.; Kulkarni, R. Development of eco-friendly polyurethane coatings based on neem oil polyetheramide. *Ind. Crops Prod.* **2013**, *50*, 550–556. [CrossRef]
3. Baroncini, E.A.; Yadav, S.K.; Palmese, G.R.; Stanzione, J.F., III. Recent advances in bio-based epoxy resins and bio-based epoxy curing agents. *J. Appl. Polym. Sci* **2016**, *133*. [CrossRef]
4. Tan, S.G.; Chow, W.S. Biobased Epoxidized Vegetable Oils and Its Greener Epoxy Blends: A Review. *Polym. Plast. Technol. Eng.* **2010**, *49*, 1581–1590. [CrossRef]
5. Ni, M.; Fong, F.; Salimon, J. Epoxidation of Palm Kernel Oil Fatty Acids. *J. Sci. Technol.* **2011**, *4*, 87–98.
6. Borugadda, V.B.; Goud, V.V. Epoxidation of Castor Oil Fatty Acid Methyl Esters (COFAME) as a Lubricant base Stock Using Heterogeneous Ion-exchange Resin (IR-120) as a Catalyst. *Energy Procedia* **2014**, *54*, 75–84. [CrossRef]
7. Salimon, J.; Haron, M.D.J.; Jahangirian, H.; Ismail, M.H.S.; Hosseini, S.; Rezayi, M.; Unit, C. Lipase Epoxidation Optimizing of Jatropha Curcas Oil Using Perlauric Acid. *Dig. J. Nanomater. Biostruct.* **2014**, *9*, 1159–1169.
8. Alam, M.; Akram, D.; Sharmin, E.; Zafar, F.; Ahmad, S. Vegetable oil based eco-friendly coating materials: A review article. *Arab. J. Chem.* **2014**, *7*, 469–479. [CrossRef]
9. Derksen, J.T.P.; Petrus Cuperus, F.; Kolster, P. Renewable resources in coatings technology: A Review. *Prog. Org. Coat.* **1996**, *27*, 45–53. [CrossRef]
10. Kashif, M.; Sharmin, E.; Zafar, F.; Ahmad, S. Synthesis and characterization of ricinoleamide-based polyurethane. *J. Am. Oil Chem. Soc.* **2011**, *88*, 1989–1996. [CrossRef]
11. Khot, S.N.; Lascala, J.J.; Can, E.; Morye, S.S.; Williams, G.I.; Palmese, G.R.; Wool, R.P. Development and application of triglyceride-based polymers and composites. *J. Appl. Polym. Sci.* **2001**, *82*, 703–723. [CrossRef]
12. Sharmin, E.; Ashraf, S.M.; Ahmad, S. Epoxidation, hydroxylation, acrylation and urethanation of Linum usitatissimum seed oil and its derivatives. *Eur. J. Lipid Sci. Technol.* **2007**, *109*, 134–146. [CrossRef]
13. Goud, V.V.; Patwardhan, A.V.; Dinda, S.; Pradhan, N.C. Kinetics of epoxidation of jatropha oil with peroxyacetic and peroxyformic acid catalysed by acidic ion exchange resin. *Chem. Eng. Sci.* **2007**, *62*, 4065–4076. [CrossRef]
14. Benyahya, S.; Aouf, C.; Caillol, S.; Boutevin, B.; Pascault, J.P.; Fulcrand, H. Functionalized green tea tannins as phenolic prepolymers for bio-based epoxy resins. *Ind. Crops Prod.* **2014**, *53*, 296–307. [CrossRef]
15. Saurabh, T.; Patnaik, M.; Bhagt, S.L.; Renge, V.C. Epoxidation of Vegetable Oils: A Review. *Int. J. Adv. Eng. Technol.* **2011**, *2*, 491–501.

16. Manthey, N.W.; Cardona, F.; Aravinthan, T. Cure kinetic study of epoxidized hemp oil cured with a multiple catalytic system. *J. Appl. Polym. Sci.* **2012**, *125*, 511–517. [CrossRef]

17. Cai, S.; Wang, L. Epoxidation of Unsaturated Fatty Acid Methyl Esters in the Presence of SO3H-functional Brønsted Acidic Ionic Liquid as Catalyst. *Chin. J. Chem. Eng.* **2011**, *19*, 57–63. [CrossRef]

18. Ikhuoria, E.U.; Obuleke, R.O.; Okieimen, F.E. Studies on the Kinetics of Epoxidation of the Methyl Esters of Parkia Biglobosa Seed Oil. *J. Macromol. Sci. Part A Pure Appl. Chem.* **2007**, *44*, 235–238. [CrossRef]

19. Saurabh, T.; Patnaik, M.; Bhagat, S.L.; Renge, V.C. Studies on Synthesis of Biobased Epoxide Using Cottonseed Oil. *Int. J. Adv. Eng. Res. Stud.* **2012**, *1*, 279–284.

20. Dinda, S.; Patwardhan, A.V.; Goud, V.V.; Pradhan, N.C. Epoxidation of cottonseed oil by aqueous hydrogen peroxide catalysed by liquid inorganic acids. *Bioresour. Technol.* **2008**, *99*, 3737–3744. [CrossRef]

21. Musante, R.L.; Grau, R.J.; Baltanás, M.A. Kinetic of liquid-phase reactions catalyzed by acidic resins: The formation of peracetic acid for vegetable oil epoxidation. *Appl. Catal. A* **2000**, *197*, 165–173. [CrossRef]

22. Sinadinović-Fišer, S.; Janković, M.; Borota, O.M. Epoxidation of castor oil with peracetic acid formed in situ in the presence of an ion-exchange resin. *Chem. Eng. Process.* **2012**, *62*, 106–113. [CrossRef]

23. Leveneur, S.; Zheng, J.; Taouk, B.; Burel, F.; Wärnå, J.; Salmi, T. Interaction of thermal and kinetic parameters for a liquid-liquid reaction system: Application to vegetable oils epoxidation by peroxycarboxylic acid. *J. Taiwan Inst. Chem. Eng.* **2014**, *45*, 1449–1458. [CrossRef]

24. Abdullah, B.M.; Salih, N.; Salimon, J. Optimization of the chemoenzymatic mono-epoxidation of linoleic acid using D-optimal design. *J. Saudi Chem. Soc.* **2014**, *18*, 276–287. [CrossRef]

25. Oyama, S.T. Rates, Kinetics, and Mechanisms of Epoxidation: Homogeneous, Heterogeneous, and Biological Routes. Mech. Homogeneous Heterog. Epoxidation Catal. 2008. Available online: http://www.elsevier.com.my/ (accessed on 20 September 2014).

26. Goud, V.V.; Dinda, S.; Paatwardhan, A.V.; Pradhan, N.C. Epoxidation of Jatropha (Jatropha curcas) oil by peroxyacids. *Asia-Pasific J. Chem. Eng.* **2010**, *5*, 346–354. [CrossRef]

27. Mushtaq, M.; Tan, I.B.; Devi, C.; Majidaie, S.; Nadeem, M.; Lee, S. Epoxidation of Fatty Acid Methyl Esters derived from Jatropha oil. In Proceedings of the 2011 National Postgraduate Conference, Kuala Lumpur, Malaysia, 19–20 September 2011; Volume 11, pp. 1–4.

28. Bora, M.M.; Gogoi, P.; Deka, D.C.; Kakati, D.K. Synthesis and characterization of yellow oleander (Thevetia peruviana) seed oil-based alkyd resin. *Ind. Crops Prod.* **2014**, *52*, 721–728. [CrossRef]

29. Nyam, K.L.; Tan, C.P.; Lai, O.M.; Long, K.; Che Man, Y.B. Physicochemical properties and bioactive compounds of selected seed oils. *LWT-Food Sci. Technol.* **2009**, *42*, 1396–1403. [CrossRef]

30. Ngadi, M.; Mba, O.I.; Dumont, M.J. Palm oil: Processing, characterization and utilization in the food industry—A review. *Food Biosci.* **2015**, *10*, 26–41.

31. Andrade-tacca, C.A.; Chang, C.; Chen, Y.; Ji, D.; Wang, Y.; Yen, Y.; Chang, C. Reduction of FFA in jatropha curcas oil via sequential direct-ultrasonic irradiation and dosage of methanol/sulfuric acid catalyst mixture on esterification process. *Energy Convers. Manag.* **2014**, *88*, 1078–1085. [CrossRef]

32. Silitonga, A.S.; Masjuki, H.H.; Mahlia, T.M.I.; Ong, H.C.; Atabani, A.E.; Chong, W.T. A global comparative review of biodiesel production from jatropha curcas using different homogeneous acid and alkaline catalysts: Study of physical and chemical properties. *Renew. Sustain. Energy Rev.* **2013**, *24*, 514–533. [CrossRef]

33. Kaya, C.; Hamamci, C.; Baysal, A.; Akba, O.; Erdogan, S.; Saydut, A. Methyl ester of peanut (*Arachis hypogea* L.) seed oil as a potential feedstock for biodiesel production. *Renew. Energy* **2009**, *34*, 1257–1260. [CrossRef]

34. Issariyakul, T.; Dalai, A.K. Biodiesel Biodiesel from Vegetable Oils Biodiesel. *Renew. Sustain. Energy Rev.* **2014**, *31*, 446–471. [CrossRef]

35. Okieimen, F.E.; Pavithran, C.; Bakare, I.O. Epoxidation and hydroxlation of rubber seed oil: one-pot multi-step reactions. *Eur. J. Lipid Sci. Technol.* **2005**, *107*, 330–336. [CrossRef]

36. Lee, C.S.; Ooi, T.L.; Chuah, C.H. The effect of reaction temperature on retaining oxirane oxygen contents in the synthesis of epoxidized diethanolamides. *Am. J. Appl. Sci.* **2009**, *6*, 72–77. [CrossRef]

37. Hazmi, A.S.A.; Aung, M.M.; Abdullah, L.C.; Salleh, M.Z.; Mahmood, M.H. Producing Jatropha oil-based polyol via epoxidation and ring opening. *Ind. Crops Prod.* **2013**, *50*, 563–567. [CrossRef]

38. Leveneur, S.; Wärnå, J.; Salmi, T.; Murzin, D.Y.; Estel, L. Interaction of intrinsic kinetics and internal mass transfer in porous ion-exchange catalysts: Green synthesis of peroxycarboxylic acids. *Chem. Eng. Sci.* **2009**, *64*, 4101–4114. [CrossRef]

39. Villa De, P.A.L.; Taborda, A.F.; Montes De Correa, C. Kinetics of limonene epoxidation by hydrogen peroxide on PW-Amberlite. *J. Mol. Catal. A Chem.* **2002**, *185*, 269–277. [CrossRef]

40. Rios, L.A.; Echeverri, D.A.; Franco, A. Epoxidation of jatropha oil using heterogeneous catalysts suitable for the Prileschajew reaction: Acidic resins and immobilized lipase. *Appl. Catal. A* **2011**, *394*, 132–137. [CrossRef]

41. Anshuman, S. *Introduction to Plastic Engineering*; Elsevier: New York, NY, USA, 2018; Chapter 3; pp. 49–110.

42. FDA Regulations on Bisphenol A (BPA). Use in Food Contact Application. Available online: https://www.fda.gov/food/food-additives-petitions/bisphenol-bpa-use-food-contact-application#regulations (accessed on 29 September 2019).

43. Dotan, A. *Handbook of Thermoset Plastics*; Dodiuk, H., Goodman, S.H., Eds.; William Andrews: San Diego, CA, USA, 2014; Chapter 15.

44. Markets, M.A. Epoxidized Soybean Oil Market by Raw Material, by Applications, by End-Use Industry, by Region-Global Trends and Forecast to 2020: Markets and Markets, 14 September 2015. Available online: https://www.prnewswire.com/news-releases/epoxidized-soybean-oil-market-by-raw-material-by-application--by-end-use-industry--by-region---global-trends-and-forecasts-to-2020-300142755.html (accessed on 1 January 2020).

45. Available online: https://www.arkema.com/en/markets-and-solutions/solutions/biobased/ (accessed on 29 September 2019).

46. Samper, M.D.; Petrucci, R.; Sanchez-Nacher, L.; Balart, R.; Kenny, J.M. New Environmentally friendly composite laminates with epoxidized linseed oil (ELO) and slate fiber fabrics. *Compos. Part B Eng.* **2015**, *71*, 203–209. [CrossRef]

47. Cavusoglu, J.; Cayli, G. Polymerization reactions of epoxidized soybean oil and maleate esters of oil-soluble resoles. *J. Appl. Polym. Sci.* **2015**, *132*, 41457. [CrossRef]