

## PHYSICOCHEMICAL, STRUCTURAL AND MECHANICAL EVALUATION OF BIO-BASED EPOXIDIZED JATROPHA OIL BLENDED WITH AMINE-CURED EPOXY RESIN AS NEW HYBRID MATRIX

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### Abstract

The utilization of bio-resources in the composite system, as an alternative to replace petroleum resources, increases tremendously due to the awareness of the society towards the environmental friendly composite material. The present work conveys the characteristics and performance of bio-epoxy resin blended with the existing polymer matrices, which was synthetic epoxy, as a new innovation to the bio-composite system. Initially, the bio-epoxy resin produced from in-situ epoxidation of Crude Jatropha Oil (CJO) in presence of ion exchange resins, Amberlite IR-120. Then, the hybrid matrix specimens were prepared by blending the Bio epoxy resin with the synthetic epoxy resin with a different mass percentage of 0%, 25%, 50%, 75%, and 100%. In addition, physicochemical, spectroscopic, tensile and flexural characterization of CJO and bio epoxy resin were also conducted. The formulation of synthetic resin with 25 wt% of bio-epoxy shows the best mechanical properties of tensile and flexural. Thus, bio-based epoxidized crude Jatropha oil is suggested as a potential green material to partially replaced the petrochemical-based resins as a polymeric matrix.

Keywords: Blends, Characterization, Jatropha oil, Performance, Renewable source, Resins.

## 1. Introduction

Synthetic resins can be defined as resins that have been synthesized through a chemical process. The most popular and extensively used resins are epoxy resins, which are commercially used in various applications namely as coating, painting, laminating, flooring, paving [1, 2] and as matrices in fabricating composites [3]. They also play important roles in the manufacturing of bicycles, automobiles, aircraft, boats, skis, and snowboard [4].

Synthetic epoxy resins are widely used due to its excellent properties in term of adhesion, rigidity, specific strength, chemical resistance, dimensional stability, as well as high fluidity [5-9]. The most well-known petro-based products applied in the synthesis of epoxy resins are epichlorohydrin and diglycidyl ether of bisphenol-A (DGEBA). DGEBA is commonly produced by reacting epichlorohydrin with the bisphenol-A (BPA) [4]. DGEBA has been reported as the best epoxy-starting component in the production of the thermosetting resin due to its aromatic structure, which allows the excellent overall performance of the cured resins [10].

However, the usage of the bisphenol-A in the production of DGEBA has been reported to cause many harmful effects to the human health to the extent that many industries have restricted the usage of BPA, especially in the food contact products such as baby bottles [1]. Toxicity of BPA, the high cost of fossil fuel, and depletion of the petroleum resources are the factors for the industries to find alternative resources to replace the petroleum-based resins.

Recently, many researchers have introduced various types of renewable resources as the starting materials in the production of epoxy resins [11] and termed as bio-resins. Renewable resources such as vegetable oils, lignin, cellulose, starch, terpenes, chitin, chitosan, as well as derivatives of the microbial activity can be used as the starting material in synthesizing various types of resins namely alkyd resins, polyesteramide resins, polyetheramide resins, polyurethane resins, epoxy resins, and polyol resins [12-16].

According to Rafiee-Moghaddam et al. [17], epoxidation process of vegetable oils is defined as a process of an addition of a single atom of oxygen to each unsaturated fatty acid chain ( $C = C$ ) by using oxidizing agents such as per-carboxylic acids, inorganic peroxides, and organic peroxides, which turns the original unsaturated fatty acid chain into an epoxy group [18]. Epoxies groups on the triglyceride backbone enable the chain to produce flexible, semi-flexible, or rigid elastomeric network structure when subjected to amine curing, UV curing, or anhydride curing.

Tan and Chow [19] explained that bio-epoxy resins are produced through epoxidation processes can be categorized into 4 types, which are conventional epoxidation or also known as Prileshajev-epoxidation process, Acidic Ion Exchange Resin (AIER) epoxidation, chemo-enzymatic epoxidation, and metal-catalysed epoxidation. The processes have been investigated at different conditions depending on the feedstock, epoxidation reagent, catalyst, and solvent [20]. Epoxidation of vegetable oils can also be performed in solution or in bulk by two reaction routes, either in situ peroxy acid or ex-situ peroxy acid. Furthermore, this process has the option to either use a heterogeneous catalyst or homogenous catalysts. However, in situ peroxy acid formation has been reported as the most

favourable process due to safety issues since concentrated peroxy acid is really unstable and explosive [18].

Bio-composites systems can be designed and engineered from two main aspects, which are the bio-matrix and bio-fibres or bio-fillers. Many research projects have been carried out to introduce the bio-composite materials by modifying the composite system in various ways. For instance, Borugadda and Goud [12] used bio-fillers obtained from the seed cakes of *Jatropha curcas L.* The bio-fillers was combined with the synthetic epoxy and polyurethane resins as polymer matrices [21]. It was found that the synthetic resins in the matrix system were able to interact with the bio-fillers, which strongly affected the mechanical properties of the bio-composite by decreasing the hardness and abrasive wear resistance.

Based on studies by Mehta et al. [22], the enhancement of the notched Izod impact strength and tensile strength of the bio-composite engineered from the non-woven fibre mat (combination of 90% hemp fibre with 10% thermoplastic polyester binder) had been reported as reinforcement with a blend of Unsaturated Polyester (UPE) resins and the functionalized vegetable oils. Meanwhile, another research was done on characterization on the bio-composite made from bio-based epoxy matrices and bio-fillers derived from the seashell wastes [15]. The research stated that the bio-fillers increased the mechanical properties of the bio-composites such as flexural modulus and hardness shore D as well as the thermal properties in term of glass transitions temperature. The bio-fillers derived from the seashell wastes, which consisted of calcium carbonate effectively increased the mechanical properties the bio-composite materials.

The epoxidized *Jatropha* oil in this work was produced through epoxidation process in the presence of ion exchange resin, Amberlite IR-120 [23]. The toxicity of phorbol esters as an anti-nutritional compound in CJO prevented its usage in the food industry, which consequently leads to no competition with the food sector. One of the purposes of this study was to establish more added value of crude *Jatropha* oil, which is a local commercial renewable resource in Malaysia. Therefore, one of the objectives of this work was to characterize ECJO in term of spectroscopy and physicochemical properties.

A lot of researches were done regarding the production of bio-resins. However, a little concern was paid to produce commercially a pure (100%) bio-resins because of its low oxirane value that resulted in poor properties of the bio-based system [19]. Thus, there is expanding research on the blending of the petrochemical-based epoxides with EVO in the presence of a variety of curing agents in order to produce excellent properties of bio-based epoxies systems. Other than that, researchers also focus on the properties of the bio-fillers or bio-fibres in order to enhance the properties of the bio-composite. Generally, synthetic resins are widely available in commercialized products. Despite its long industrial success, synthetic resins had caused many health and environmental problems. These indicated a need to introduce bio-resins to the industries to support the growth of renewable and sustainable earth.

As a consequence, this paper sought to propose a combination of the synthetic epoxy resin with the bio-epoxy resin in order to produce a blend cured polymer matrix in the bio-composite system. Another aim of this work was to replace an increasing amount of synthetic resins with different contents of bio-based epoxidized crude *Jatropha* oil. The blend-cured polymer was then subjected to mechanical tests to

determine its tensile and flexural properties. This work could broaden the range of application of bio-epoxy resins as a matrix in the bio-composite system.

## 2. Materials and Methods

The materials that were used in this research were crude *Jatropha* oil (CJO) was purchased from BATC Development Berhad (Kuala Lumpur, Malaysia), glacial acetic acid ( $\text{CH}_3\text{COOH}$ ) from Fisher Scientific (Shah Alam, Malaysia), anhydrous sodium sulphate ( $\text{Na}_2\text{SO}_4$ ) from R&M Chemicals Ltd (Semenyih, Malaysia), and 30% hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and Amberlite IR-120 from Sigma-Aldrich (Subang Jaya, Malaysia).

### 2.1. Synthesis of bio-epoxy resins

The epoxidation of CJO was carried out in a batch mode in a glass reactor consisting of three-necked 1 L round bottom flask. An analogue overhead Teflon stirrer was inserted in the reactor through the central neck while another neck was used to place a thermometer. The third neck was used for dropping the raw materials into the reactor. The reactor was heated by a controlled temperature water bath within  $\pm 1$  °C of the desired temperature. The method employed for the synthesis of bio-epoxy resins from CJO was the epoxidation of oil with AEIR as previously reported [23-25].

### 2.2. Preparation and curing of the ECJO/epoxAmite resins

A mould made of aluminium with dimensions 228×22×25.4 mm was used for the casting of the cured epoxy blends. Mirror glaze wax (Meguiars) was used for wiping the inside surface and walls of the mould in order to avoid the adhesion between the cured epoxy resins and the aluminium mould. Five different ratios (A, B, C, D and E) were used for casting the blends of the epoxy resins. The required mixture of EpoxAmite@100, ECJO and Hardener 103 were made by mixing them in the Epoxy Equivalent Weight (EEW) ratio of 190:263.16:54.

Each sample was weighed in a small container before mixing manually. The blend of the polymer was initially prepared by mixing the synthetic resins and bio-epoxy resins at room temperature, stirring with a magnetic stirrer for about 10 min until it became homogenous. Then, the amount of hardener as shown in Table 1 was added into the mixture and stirred for another 10 min. The final mixture was then carefully poured into the mould-wax surface by ensuring that there was no air entrapped inside the mixture. The amount of blend for the polymers shown in Table 1 was varied in mass percentage ratio but the total mass of polymers was kept as 460 g in order to provide 10 mm of the height of the cured blend matrix for mechanical tests purposes.

Each specimen was initially cured for 24 h at room temperature, which was then followed by different post-curing processes based on the percentage ratio of the synthetic resins in the mixture as shown in Table 2. The specimens were considered fully cured when it could come out from the mould in a good shape and when the surface of the specimen was touched; it did not leave any sticky liquid mixture on the fingertip. The fully cured specimens were cut into predetermined sizes by using a vertical saw machine (Metabo, BAS 260 swift), which was then tested for tensile and flexural properties.

**Table 1. Mass calculation of synthetic resin, bio-epoxy resins and hardener.**

Specimen name	Mass percentage (%)		EpoxAmite® 100 (g)	ECJO (g)	Mass of hardener (g)		
	Resin	ECJO			For resin <sup>a</sup>	For ECJO <sup>b</sup>	Total
A	100	0	460	0	130.74	0	130.7
B	75	25	345	115	98.05	14.16	112.2
C	50	50	230	230	65.37	28.32	93.69
D	25	75	115	345	32.68	42.48	75.16
E	0	100	0	460	0	56.61	56.61

<sup>(a)</sup> Hardener was calculated based on the epoxy equivalent weight (g) ratio 190:54 of EpoxAmite to Hardener 103.

<sup>(b)</sup> Presence of epoxy group in bio-epoxy resins was calculated by multiplying the mass of bio-epoxy resins with 60% of the degree of epoxidation.

Hardener was calculated based on the epoxy equivalent weight (g) ratio 263.16:54 of ECJO to Hardener 103.

**Table 2. Conditions of the curing and post-curing process**

Specimen name	Initial curing process	Post-curing process			
		2 h at 6 °C	3 h at 80 °C	3 h at 100 °C	3 h at 120 C
A	24 h at RT	√	√	√	√
B	24 h at RT	√	√	√	√
C	24 h at RT	√	√	√	√
D	24 h at RT	√	√	√	X
E	24 h at RT	√	√	X	X

**2.3. Iodine value (IV) determination**

Iodine value (IV) test is a measure of unsaturated carbons present in the compound. It was determined using the Lubrizol Test Procedure TP-AATM-112-01. This test measured the conversion of the double bond into oxirane indirectly [17] as shown in Eq. (1).

$$\% \text{ Conversion of double bonds} = \frac{(IV_{initial} - IV_{final})}{(IV_{initial})} \times 100 \tag{1}$$

where  $IV_{initial}$  (g I<sub>2</sub>/100 g) is iodine value of the oil sample before epoxidation process and  $IV_{final}$  (g I<sub>2</sub>/100 g) is the iodine value of the epoxy sample after epoxidation process.

**2.4. Oxirane oxygen content (OOC) determination**

Oxirane Oxygen Content (OOC) test is a measure of the oxygen atom present in the epoxy group. OOC values obtained from the OOC test in the laboratory directly represented the conversion of the double bond of the fatty acids. The values of OOC represented the amount of Double Bond (DB) converted to the epoxides through epoxidation reaction. The higher value of OOC presented the higher conversion of the double bond into the oxirane ring. The test was performed after the sample was dried for 12 h in an oven in order to ensure complete removal of water. The theoretical OOC was determined to be 6.13% by using the expression represented in Eq. (2)

$$\text{Oxirane Oxygen content, } OOC_{the} (\%) = \left( \frac{\frac{IV_0}{2A_1}}{100 + \left(\frac{IV_0}{2A_1}\right)A_0} \right) A_0 \times 100 \tag{2}$$

where  $OO_{\text{the}}$  (g/100 g sample) is theoretically oxirane oxygen content in 100 g of epoxides,  $IV_o$  (g  $I_2$ /100 g) is Initial iodine value,  $A_i$  (u) is the atomic weight of iodine (126.9) and  $A_o$  (u) is the atomic weight of oxygen (16).

The experimental  $OO$  ( $OO_{\text{exp}}$ ) was determined through a direct titration method of hydrobromic acid in the acetic acid solution according to the AOCS Official Method Cd 9-57 [26]. Then, the experimental oxirane oxygen content,  $OO_{\text{exp}}$  (%) was calculated as shown in Eq. (3). After that, the percentage relative conversion to oxirane (% RCO) value was taken as the response variable, which was calculated by taking the percentage of the ratio  $OO_{\text{exp}}$  over  $OO_{\text{the}}$  as explained in Eq. (4)

$$\text{Oxirane Oxygen content, } OO_{\text{exp}} (\%) = \frac{\text{Titration} \times 0.1 \text{ N HBr} \times 1.60}{\text{Weight of sample}} \quad (3)$$

$$\text{Relative Conversion to Oxirane, RCO} (\%) = \frac{OO_{\text{exp}}}{OO_{\text{the}}} \times 100 \quad (4)$$

where  $OO_{\text{exp}}$  (g/100 g sample) is the experimental oxirane oxygen content measured based on the standard official method.

## 2.5. Dynamic viscosity determination

The dynamic viscosity of ECJO was measured according to the American Society for Testing and Materials (ASTM) D445-15a manual using a Brookfield DV2T viscometer with a plate spindle at room temperature of 25 °C. The value was compared to the CJO's dynamic viscosity.

## 2.6. FTIR spectroscopy characterization

The CJO and ECJO were tested for FTIR Spectroscopy by using FTIR Spectrum 100 (PerkinElmer) in the range of 4000-600  $\text{cm}^{-1}$  to identify the functional groups present in the compound. Then, both spectra were compared.

## 2.7. NMR spectroscopy characterization

The  $^1\text{H}$ NMR and  $^{13}\text{C}$ NMR spectroscopy of CJO and ECJO were recorded using NMR 400MHz (PerkinElmer) with chloroform (Sigma-Aldrich) as a solvent. The spectra for each of the sample were analysed in the range of 0-200 ppm by using Delta 5.0.4 software [27] and compared against each other.

## 2.8. Tensile test

Tensile property of the cured blend polymer was performed with INSTRON 3382 machine in accordance with ISO 527 with a crosshead speed of 4 mm/min. Five pieces for each specimen were cut in a rectangular shape of dimension 220 mm long and 25 mm wide with 10 mm thickness for the measurement of tensile strength and tensile modulus. All pieces of the specimens were kept in a closed plastic bag prior to test. Analysis of the specimens was done by comparing the blended specimens with the pure cured synthetic resins.

## 2.9. Flexural test

The flexural test was conducted using INSTRON 3365 machine in accordance to ISO 178 with a crosshead speed 4 mm/min. All matrices were cut prior to test by using a vertical saw machine to a standard rectangular size of 220 mm long and 20

mm wide with 10 mm thickness. The specimens kept in a closed plastic bag prior to the test. Flexural properties of the bio-hybrid matrix were compared with the pure cured synthetic matrix.

### 3. Results and Discussion

#### 3.1. Physico-chemical properties of CJO and ECJO

The physicochemical properties of CJO and ECJO were compared in terms of iodine value (IV), density, dynamic viscosity, and kinematic viscosity. Table 3 shows that CJO has a high iodine value of 103.63 g I<sub>2</sub>/100 g, which is similar to the 103.62 g I<sub>2</sub>/100 g [28]. It indicates that CJO has a high level of fat unsaturation and is a high reactivity compound. In correlation to that, vegetable oils that possess high iodine value are the most preferable in the epoxidation due to high production of epoxides [29]. The iodine value can directly determine the amount of carbon double bond present and the value of oxirane produced indirectly. Meanwhile, the oxirane oxygen test can determine the amount of oxirane produced directly. These two properties can be used to compare the final percentage of oxirane produced.

According to Table 3, the iodine value decreased from 103.63 g I<sub>2</sub>/100 g (CJO) to 42.17 g I<sub>2</sub>/100 g (ECJO), which resulted in 59.31 % conversion of the double bonds. Likewise, the oxirane content gave 60.55 % conversion of the double bonds with the oxirane content of 3.71 % in ECJO. Thus, the difference between the results was only 1.24 %, which might have come from experimental errors such as some products lost during the washing step after the epoxidation reaction. The density of ECJO is higher than CJO due to the addition of the oxygen atom in the compound, which results in the increment in the molecular weight of the compound [30]. The viscosity value obtained from the viscometer is called as dynamic viscosity, or also known as absolute viscosity. The kinematic viscosity is calculated by taking the ratio of dynamic viscosity over density. As can be seen from Table 3, the dynamic and kinematic viscosity values of ECJO are higher than CJO. The high value for both properties of the viscosity might come from the high number of the hydroxyl group in ECJO, which introduces an intermolecular hydrogen bonding in the compound, resulting in the interactions between molecules become stronger [30].

**Table 3. Physico-chemical properties of CJO and ECJO.**

Parameter	CJO		ECJO
	This study	Borugadda and Goud [12]	This study
Iodine value (g I <sub>2</sub> /100g)	103.63	103.62	42.17
Conversion of double bonds (%)	-	-	59.31
Relative Conversion to Oxirane, RCO (%)	-	-	60.55
Oxirane Oxygen content, OOC (%)	-	-	3.71
Density (g/cm <sup>3</sup> )	0.893	0.903	1.298
Dynamic viscosity at 25 °C (cP)	46.8	42.88	546
Kinematic viscosity at 25 °C (cSt)	52.41	47.49	588
Physical state at room temperature	Liquid	Liquid	Liquid

#### 3.2. FTIR analysis of CJO and ECJO

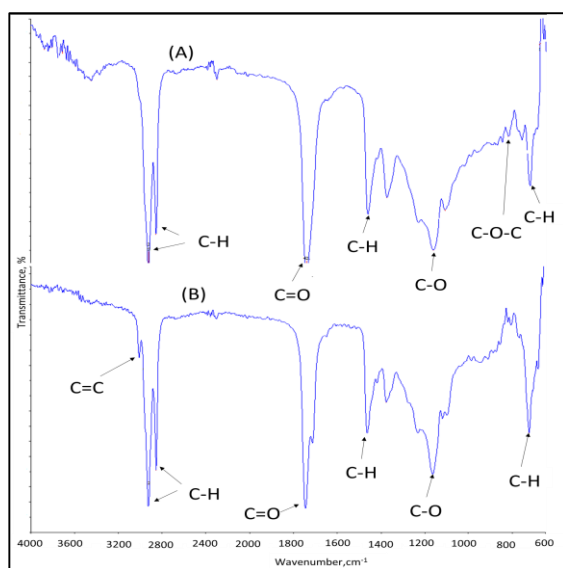
The changes in the functional groups after the epoxidation reaction are shown in Fig. 1. The figures are (a) CJO spectra, and (b) ECJO spectra. Table 4 shows the main wavelengths for the FTIR functional groups in the compounds.

Each peak corresponds to each different functional group. Figure 1(A) illustrates the peaks for the unsaturated alkene (C-H) at 3008  $\text{cm}^{-1}$  in the CJO compound. The disappearance of the double bond in the ECJO compound from the spectra and appearance of new peaks at 822  $\text{cm}^{-1}$  confirmed the synthesis of the epoxides. This result was in line with the previous works that reported the band of oxirane formed in the range of 820-843  $\text{cm}^{-1}$  [1, 31, 32].

However, it is apparent from Fig. 1(B) that the peak of the oxirane ring (C-O-C) was not very significant due to the low percentage of epoxy contents in ECJO. This low peak correlated with the analytical test of OOC which was only 60.55 %. The absence of the hydroxyl peaks in the range of 3000-3500  $\text{cm}^{-1}$  (O-H) in the ECJO compound proved that the minimum oxirane decomposition occurred in the epoxidation reaction [33]. Thus, the absence of the oxirane cleavage after 5 h of reaction was confirmed.

**Table 4. FTIR of CJO and ECJO.**

A. Wavelength CJO ( $\text{cm}^{-1}$ )	B. Wavelength ECJO ( $\text{cm}^{-1}$ )	Functional group	References
3008	-	C=C bending vibration (aliphatic carbon)	
29, 252, 855	2926, 2855	C-H stretching vibration (aliphatic carbon)	
1745	1742	C=O stretching frequency of ester	Abdullah et al. [1], Ikhuoria et al. [31] and Okieimen et al. [32]
1463	1462	C-H bending frequency of unsaturated alkene	
1163	1165	C-O stretching frequency of ester	
-	822	C-O-C oxirane ring	
723	724	C-H group vibration (aliphatic)	



**Fig. 1. FTIR peak of (A) ECJO and (B) CJO.**



### 3.3. $^{13}\text{C}$ NMR analysis

The  $^{13}\text{C}$ NMR spectroscopy is one of the methods for identifying all the carbon atoms present in the organic compound by giving great distinctive signals in determining whether the carbon is linked to a hydrogen atom or not. It is a recent instrument in providing greater structural formation details, especially for the fatty acids compounds.

Figures 2 and 3 illustrated the  $^{13}\text{C}$ NMR spectra of the CJO and ECJO compound, respectively. The signals of C Spectroscopy with the assignment of the groups for both spectra are recorded in Table 5. The main reason for performing the  $^{13}\text{C}$ NMR spectroscopy was to check the success of the epoxidation reaction by identifying the molecular structure of the ECJO and CJO compounds.

The epoxidation was considered successful when the carbon double bonds in CJO turned into oxirane ring in the ECJO compound. Figure 2 illustrates the unsaturated carbon in the alkene region of CJO at 127.954-130.171 ppm [31].

The epoxidation reaction of CJO was confirmed by the appearance of the oxirane ring for the ECJO compound spectra as depicted in Fig. 3 at the frequency of 54.203-57.260 ppm. However, it is apparent from Fig. 2 that very few small peaks appear in ECJO compound in the 123.783- 132.664 ppm range refers to the alkene region [1].

This indicated that there were a few unreacted free carbon double bonds in the ECJO compound. This finding highlighted the experimental result of the OOC test, which recorded 60.55% oxirane content in the ECJO. This result was also consistent with the finding in the epoxidation of the linoleic acid and rubber seed oil [1, 34].

**Table 5.  $^{13}\text{C}$ NMR of CJO and ECJO.**

Frequency, $\delta$ (ppm) of CJO	Frequency, $\delta$ (ppm) ECJO	Assignment	Structural	References
14.29, 14.083	13.979-14.083	Carbon of the terminal methyl group	R-CH <sub>3</sub>	
22.734-31.972	22.654-31.926	Carbon in the FA chain (aliphatic carbon)	R-CH <sub>2</sub> -	
-	54.203-57.260	Oxirane ring	C-O-C	Abdullah et al. [1], Okieimen et al. [34] and Sharmin et al. [35]
61.373-62.223	62.097	Carbon of the glycerol	O-CH <sub>2</sub> -R	
76.906-77.412	74.459-77.481	Carbon of the glycerol	R-CH-R	
127.954-130.171	123.783-132.664	Unsaturated carbon (alkene region)	C = C	
172.819-179.276	172.762-177.484	Carbon of carbonyl group	C = O	

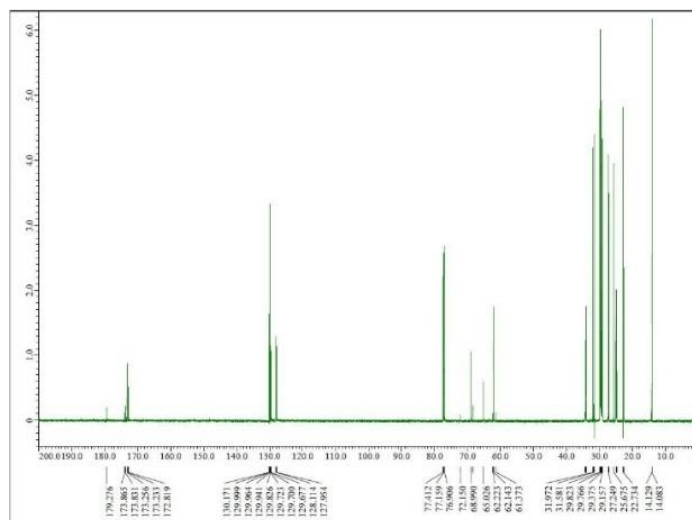


Fig. 2.  $^{13}\text{C}$ NMR spectra of CJO.

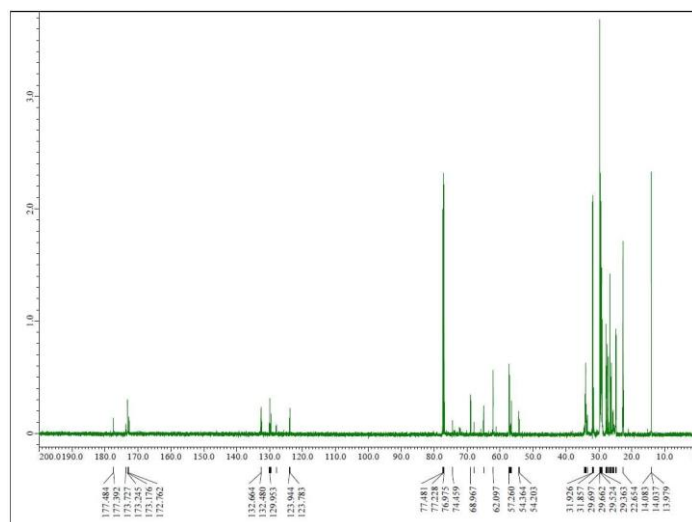


Fig. 3.  $^{13}\text{C}$ NMR Spectra of ECJO.

### 3.4. $^1\text{H}$ NMR analysis

The  $^1\text{H}$ NMR spectroscopy detects the proton atoms in a compound structure. The signals resulted from the  $^1\text{H}$ NMR spectra of CJO and ECJO are demonstrated in Figs. 4 and 5 respectively. Table 6 presents the signals of H Spectroscopy with the assignment of the group for both spectra.

The peaks of the hydrogen atoms directly bonded with carbon atoms, which form the oxirane ring can be seen at a frequency of 2.809, 3.022, and 3.031 ppm as illustrated in Fig. 5. These results were consistent with the findings of a past study, which concluded that the epoxy protons are in the range of 2.7-3.2 ppm [1].

The peaks for the molecular structure of R-CH=CH-R, which refers to the alkene region, appear in both CJO and ECJO compounds due to the proton in the methane group [31, 35]. These peaks were illustrated in Figs. 4 and 5 at  $\delta = 5.273$ - $5.323$  ppm and  $\delta = 5.17$ - $5.24$  ppm for CJO and ECJO compound, respectively.

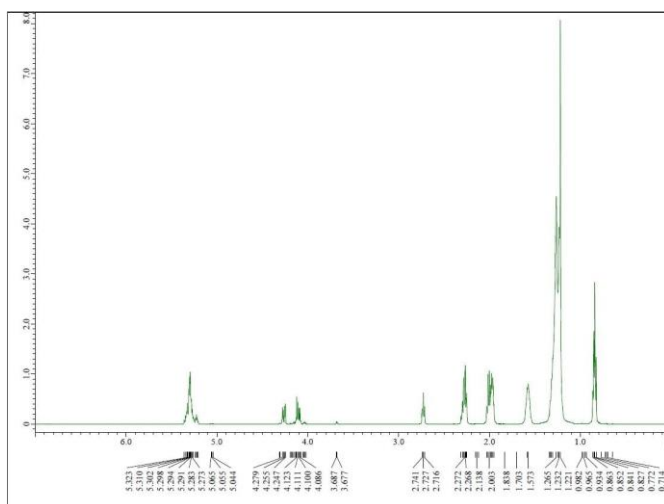
Although there were two signals in the alkene region of ECJO compound as in Fig. 5, the peaks were significantly low compared to the peaks of the alkene region in CJO compound as shown in Fig. 4. This decrement showed that most of all the carbon atoms in the double bond of the fatty acids were turned into oxirane ring with a slight amount of the unreacted free carbon atoms.

These findings correlated with the experimental result of the OOC test, which was 60.55% of the oxirane content in the ECJO. Nevertheless, these results indicated the success of the epoxidation of CJO with the appearance of the oxirane ring in the ECJO.

These results were also in line with earlier literature, which had some of the unreacted carbon double bonds in the epoxidation of the rubber seed oil [34].

**Table 6. <sup>1</sup>HNMR of CJO and ECJO**

Frequency, $\delta$ (ppm) CJO	Frequency, $\delta$ (ppm) ECJO	Assignment	Structural	References
0.714-0.863	0.772-0.825	Terminal methyl group proton signal	R-CH <sub>3</sub>	Abdullah et al. [1], Okieimen et al. [34] and Sharmin et al. [35]
1.221-1.265, 1.573, 2.003-2.741	1.165-1.209, 1.523, 1.945-2.23	Methylene proton signal	R-CH <sub>2</sub> -R	
-	2.809, 3.022, 3.031	Epoxy proton	-CH-O-CH-	
4.086-4.123	4.046-4.071	Hydrogen proton attributed from glycol segment	R-CH <sub>2</sub> -O	
4.247-4.279	4.195-4.218	Hydrogen proton attributed from glycol segment	R-CH-R	
5.273-5.323	5.17, 5.24	Methane proton	R-CH=CH-R	



**Fig. 4. <sup>1</sup>HNMR spectra of CJO.**

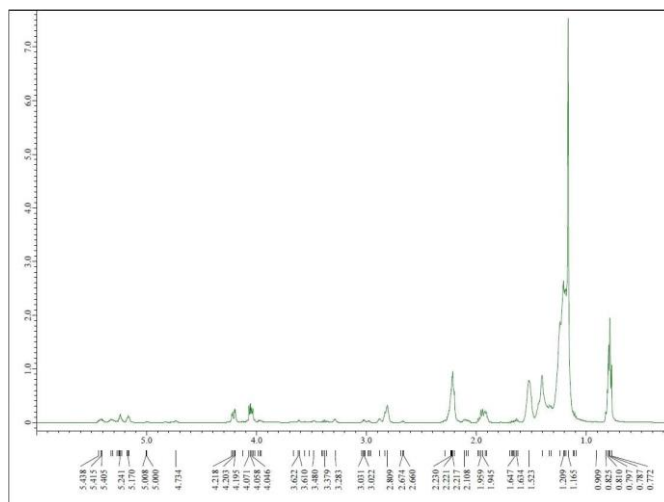


Fig. 5. <sup>1</sup>H NMR spectra of ECJO.

### 3.5. Mechanical properties

The cured blended synthetic resins with different contents of bio-based epoxy resins were subjected to mechanical tests to determine their tensile and flexural properties.

In the present tensile and flexural tests, the maximum mass percentage of ECJO in the hybrid matrix was restricted up to 50 wt% because above this ECJO mass percentage, the surface of the hybrid matrix did not completely cure under the described condition as in Table 1.

This incident may be due to inadequate synthetic-bio-resin adhesions, which lead to poor dispersion and low crosslinking network between the atoms in the matrix [19]. It was reported that poor adhesion between the oxirane ring in the backbone of ECJO and synthetic resin in the matrix system reduces the mechanical properties [36].

#### 3.5.1. Tensile strength

Tensile properties of the hybrid matrix determine its ability to resist breaking under tensile stress [37].

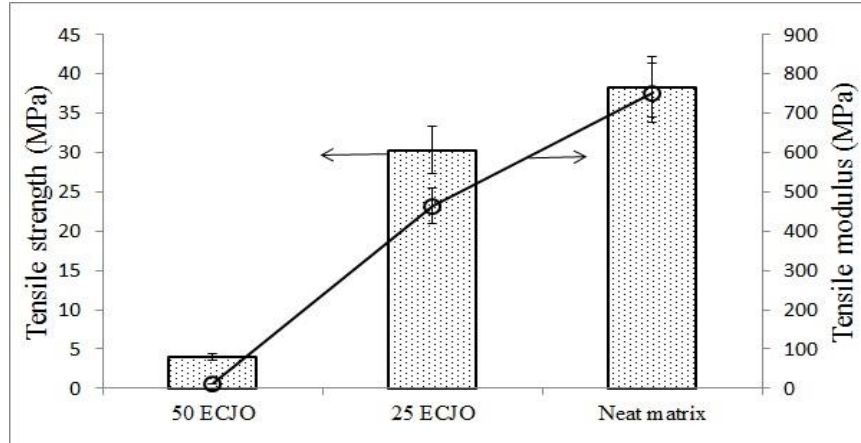
From the fracture tension and average deformation values as shown in Fig. 6 and Table 7, there is a clear reduction of the tensile strength and tensile modulus in relation to the increasing amount of ECJO mass percentage added to the system due to its ductile aliphatic long chain structure and low crosslink density [38].

As similarly reported in a study of Johnson et al. [39], however, the hybrid bio-matrix with 25 wt% of the ECJO, showed the closest values of tensile strength and tensile modulus to the neat matrix. This result interpreted that a small amount of the bio-resin was compatible to blend in the network structure.

Thus, it is suggested that a replacement of synthetic resins with the bio-synthetic resin in the bio-composite systems is possible and comparably good with a commercially available matrix.

**Table 7. Tensile test.**

System	Strain at break (MPa)	Deformation at fracture (%)	Modulus of elasticity (MPa)
Neat matrix	37.42±0.12	9.50±0.50	5.10±1.24
25% ECJO	28.85±2.25	8.50±0.50	3.79±1.79
50% ECJO	4.23±0.19	110.00±5.00	0.45±0.14



**Fig. 4. Tensile strength and tensile modulus of cured blended ECJO with synthetic resin.**

**3.5.2. Flexural strength**

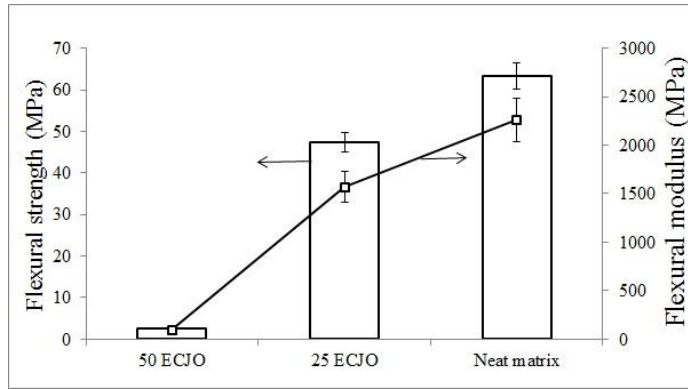
Flexural properties describe the elongation at break values where observation and calculation are made when longitudinal stress/load are applied to the hybrid matrix [37].

As observed in Fig. 7 and Table 8, the average flexure and deformation values at the fracture decreased in relation to the increased amount of ECJO mass percentage added to the system. The obtained data are in agreement with the tensile tests. This is similar to the results obtained by Manthey et al., who found results for epoxidized hemp oil based bio-resins with the reinforcement of jute fibre [27].

It can be noticed that the 25 wt% of ECJO in the hybrid matrix displayed the highest flexural strength and flexural modulus compared to the 50 wt% of ECJO in the hybrid matrix. This can be reasonably ascribed to their physical appearances, which were stiff and rigid. Hence, at a concentration of 25%, the ECJO sample displayed comparable performance to the neat matrix. It can be concluded that utilisation of the bio-resin blends is possible in the bio-composite system.

**Table 8. Flexural test**

System	Strain at break (MPa)	Deformation at fracture (%)	Modulus of elasticity (MPa)
Neat matrix	63.25±3.00	4.5±0.5	20.92±1.22
25% ECJO	46.39±1.81	5±0.5	13.29±0.67
50% ECJO	2.52±0.25	6.5±0.5	1.04±0.04



**Fig. 5. Flexural strength and modulus of cured blended ECJO with synthetic resin.**

#### 4. Conclusions

Following the analysis of the results, it can be concluded that improvements in some properties are frequently followed by a decreased in other properties. Some of the conclusions are deduced from this research are written as the following:

- The chemical analysis of ECJO obtained in the OOC test showed that 60.55% of the double bonds in CJO were converted into the oxirane ring.
- The result was also supported by the FTIR,  $^{13}\text{C}$ NMR, and  $^1\text{H}$ NMR spectroscopy, which exhibited the presence of the epoxy ring in the range of  $822\text{ cm}^{-1}$ ,  $54.203\text{-}57.260\text{ ppm}$ , and  $2.809\text{-}3.031\text{ ppm}$  respectively.
- The physical state of the ECJO was found to be more viscous compared to the CJO due to the increased density from the addition of the oxygen atoms after the epoxidation reaction.
- Bio-epoxy resins can be used in the bio-composite system since it is possible to produce a hybrid bio-matrix by blending the ECJO with the synthetic resin.
- It is worth pointing out here that the values of tensile and flexural properties of the 25 wt% ECJO in the bio-matrix were not so far from the neat matrix: The 25 wt% ECJO/EpoxAmitte had tensile strength  $30.29\pm 2.25\text{ MPa}$  (vs neat matrix  $38.32\pm 3.16\text{ MPa}$ ), modulus of elasticity  $3.79\pm 1.79\text{ MPa}$  ( $5.10\pm 1.24\text{ MPa}$ ), flexural strength  $47.44\pm 2.57\text{ MPa}$  ( $63.25\pm 7.52\text{ MPa}$ ), and modulus of elasticity  $13.29\pm 0.67\text{ MPa}$  ( $20.92\pm 1.22\text{ MPa}$ ).
- This evidently proved the possibility of intermolecular interactions between the oxirane ring in the ECJO and synthetic resins in the matrix network in this present study.
- In terms of the performance, the formulation with 25 wt% ECJO exhibited the best set of tensile and flexural properties with the added benefit of being an environmentally friendly bio-composite, which is better than petroleum-based epoxy resins.
- In future research, the formulation 10-25 wt% of the ECJO can be used to promote the implementation of bio-epoxy resin in the bio-composite system.
- Further studies can also focus on the production of genuine bio-composite by incorporating plant fibres (such as flax, bagasse, and sisal) as reinforcement in the bio-matrix network, which would enhance the performance of the final bio-

composite produced. All these efforts were done to achieve the main purpose of green technology, which is by reducing the dependency on petrochemical-based resins.

### Nomenclatures

*Ppm*        Parts per millions

### Greek Symbols

$\delta$          Frequency

### Abbreviations

AEIR	Acidic Ion Exchange Resin
BPA	Bisphenol-A
CJO	Crude Jatropha Oil
DGEBA	Diglycidyl Ether of Bisphenol-A
ECJO	Epoxidized Crude Jatropha Oil
EEW	Epoxy Equivalent Weight
EVO	Epoxidized Vegetable Oil
IV	Iodine Value
OOO	Oxirane Oxygen Content
RCO	Relative Conversion to Oxirane
UPE	Unsaturated Polyester

### References

1. Abdullah, B.M.; Salih, N.; and Salimon, J. (2014). Optimization of the chemoenzymatic mono-epoxidation of linoleic acid using D-optimal design. *Journal of Saudi Chemical Society*, 18(3), 276-287.
2. Alam, M.; Akram, D.; Sharmin, E.; Zafar, F.; and Ahmad, S. (2014). Vegetable oil based eco-friendly coating materials: A review article. *Arabian Journal of Chemistry*, 7(4), 469-479.
3. Benyahya, S.; Aouf, C.; Caillol, S.; Boutevin, B.; Pascault, J.P.; and Fulcrand, H. (2014). Functionalized green tea tannins as phenolic prepolymers for bio-based epoxy resins. *Industrial Crops and Products*, 53, 296-307.
4. Jin, F.-L.; Li, X.; and Park, S.-J. (2015). Synthesis and application of epoxy resins: A review. *Journal of Industrial and Engineering Chemistry*, 29, 1-11.
5. Boruah, M.; Gogoi, P.; Adhikari, B.; and Dolui, S.K. (2012). Preparation and characterization of Jatropha curcas oil based alkyd resin suitable for surface coating. *Progress in Organic Coatings*, 74(3), 596-602.
6. Chen, Y.-H.; Chiang, T.-H.; and Chen, J.-H. (2012). An optimum biodiesel combination: Jatropha and soapnut oil biodiesel blends. *Fuel*, 92(1), 377-380.
7. Ferdosian, F.; Zhang, Y.; Yuan, Z.; Anderson, M.; and Xu, C. (2016). Curing kinetics and mechanical properties of bio-based epoxy composites comprising lignin-based epoxy resins. *European Polymer Journal*, 82, 153-165.
8. Gonçalves, J.A.V.; Campos, D.A.T.; Oliveira, G.d.J.; Rosa, M.d.L.d.S.; and Macedo, M.A. (2014). Mechanical properties of epoxy resin based on granite stone powder from the sergipe fold-and-thrust belt composites. *Material Research*, 17(4), 878-887.

9. Hirose, S.; Hatakeyama, T.; and Hatakeyama, H. (2012). Novel epoxy resins derived from biomass components. *Procedia Chemistry*, 4, 26-33.
10. Pawar, M.; Kadam, A.; Yemul, O.; Thamke, V.; and Kodam, K. (2016). Biodegradable bioepoxy resins based on epoxidized natural oil (cottonseed and algae) cured with citric and tartaric acids through solution polymerization: A renewable approach. *Industrial Crops and Products*, 89, 434-447.
11. Ferri, E.; and Talentino, D. (2011). Bio-resins from cashew nutshell oil. *Reinforced Plastics*, 55(3), 29-31.
12. Borugadda, V.B.; and Goud, V.V. (2014). 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*, 54, 75-84.
13. Chaudhari, A.; Gite, V.; Rajput, S.; Mahulikar, P.; and Kulkarni, R. (2013). Development of eco-friendly polyurethane coatings based on neem oil polyetheramide. *Industrial Crops and Products*, 50, 550-556.
14. Dinda, S.; Patwardhan, A.V.; Goud, V.V.; and Pradhan, N.C. (2008). Epoxidation of cottonseed oil by aqueous hydrogen peroxide catalysed by liquid inorganic acids. *Bioresource Technology*, 99(9), 3737-3744.
15. Fombuena, V.; Bernardi, L.; Fenollar, O.; Boronat, T.; and Balart, R. (2014). Characterization of green composites from biobased epoxy matrices and bio-fillers derived from seashell wastes. *Materials and Design*, 57, 168-174.
16. Gandini, A.; and Lacerda, T.M. (2015). From monomers to polymers from renewable resources: Recent advances. *Progress in Polymer Science*, 48, 1-39.
17. Rafiee-Moghaddam, R.; Salimon, J.; Haron, M.D.J.; Jahangirian, H.; Ismail, M.H.S.; Hosseini, S.; and Rezayi, M. (2014). Lipase epoxidation optimizing of jatropha curcas oil using perlauric acid. *Digest Journal of Nanomaterials and Biostructures*, 9(3), 1159-1169.
18. Sinadinovic-Fiser, S.; Jankovic, M.; and Borota, O. (2012). Epoxidation of castor oil with peracetic acid formed in situ in the presence of an ion-exchange resin. *Chemical Engineering and Processing: Process Intensification*, 62, 106-113.
19. Tan, S.G.; and Chow, W.S. (2010). Biobased epoxidized vegetable oils and its greener epoxy blends: A review. *Polymer-Plastics Technology and Engineering*, 49(15), 1581-1590.
20. Goud, V.V.; Patwardhan, A.V.; Dinda, S.; and Pradhan, N. C. (2007). Kinetics of epoxidation of jatropha oil with peroxyacetic and peroxyformic acid catalysed by acidic ion exchange resin. *Chemical Engineering Science*, 62(15), 4065-4076.
21. Valasek, P. (2015). Mechanical properties of polymer composites based on bio-particles (Jatropha curcas L). *Jurnal Teknologi*, 76(3), 1-5.
22. Mehta, G.; Mohanty, A.K.; Misra, M.; and Drzal, L.T. (2004). Biobased resin as a toughening agent for biocomposites. *Green Chemistry*, 6(5), 254-258.
23. Goud, V.V.; Dinda, S.; Paatwardhan, A.V.; and Pradhan, N.C. (2010). Epoxidation of Jatropha (Jatropha curcas ) oil by peroxyacids. *Asia-Pacific Journal of Chemical Engineering*, 5(2), 346-354.
24. Mushtaq, M.; Tan, I.M.; Nadeem, M.; Devi, C.; Lee, S.Y.C.; Sagir, M.; and Rashid, U. (2013). Epoxidation of methyl esters derived from Jatropha oil: An optimization study. *Grasas y Aceites*, 64(1), 103-114.



25. Rios, L.A.; Echeverri, D.A.; and Franco, A. (2011). Epoxidation of Jatropha oil using heterogeneous catalysts suitable for the Prileschajew reaction: Acidic resins and immobilized lipase. *Applied Catalysis A: General*, 394(1-2), 132-137.
26. Paquot, C. (1979). *Standard methods for the analysis of oils, fats, and derivatives* (6<sup>th</sup> ed.). Oxford: Pergamon Press.
27. Manthey, N.W.; Cardona, F.; Francucci, G.; and Aravinthan, T. (2013). Thermo-mechanical properties of epoxidized hemp oil-based bioresins and biocomposites. *Journal of Reinforced Plastics and Composites*, 32(19), 1444-1456.
28. Akbar, E.; Yaakob, Z.; Kamarudin, S.K.; Ismail, M.; and Salimon, J. (2009). Characteristic and composition of jatropha curcas oil seed from Malaysia and its potential as biodiesel feedstock. *European Journal of Scientific Research*, 29(3), 396-403.
29. Nyam, K.L.; Tan, C.P.; Lai, O.M.; Long, K.; and Che Man, Y.B. (2009). Physicochemical properties and bioactive compounds of selected seed oils. *LWT - Food Science and Technology*, 42(8), 1396-1403.
30. Sammaiah, A.; Padmaja, K.V.; and Prasad, R.B.N. (2014). Synthesis of epoxy jatropha oil and its evaluation for lubricant properties. *Journal of Oleo Science*, 63(6), 637-643.
31. Ikhuria, E.U.; Obuleke, R.O.; and Okieimen, F.E. (2007). Studies on the kinetics of epoxidation of the methyl esters of Parkia Biglobosa seed oil. *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, 44(2), 235-238.
32. Okieimen, F.E.; Bakare, O.I.; and Okieimen, C.O. (2002). Studies on the epoxidation of rubber seed oil. *Industrial Crops and Products*, 15(2), 139-144.
33. Hong, L.K.; Yusop, R.M.; Salih, N.; and Salimon, J. (2015). Optimization of the in situ epoxidation of linoleic acid of Jatropha curcas Oil with Performic Acid. *The Malaysian Journal of Analytical Sciences*, 19(1), 144-154.
34. Okieimen, F.E., Pavithran, C.; and Bakare, I.O. (2005). Epoxidation and hydroxylation of rubber seed oil: One-pot multi-step reactions. *European Journal of Lipid Science and Technology*, 107(5), 330-336.
35. Sharmin, E.; Ashraf, S.M.; and Ahmad, S. (2007). Epoxidation, hydroxylation, acrylation and urethanation of Linum usitatissimum seed oil and its derivatives. *European Journal of Lipid Science and Technology*, 109(2), 134-146.
36. Deka, H.; Mohanty, A.; and Misra, M. (2014). Renewable-resource-based green blends from Poly(furfuryl alcohol) bioresin and lignin. *Macromolecular Materials and Engineering*, 299(5), 552-559.
37. Saba, N.; Paridah, M.T.; Abdan, K.; and Ibrahim, N.A. (2016). Effect of oil palm nano filler on mechanical and morphological properties of kenaf reinforced epoxy composites. *Construction and Building Materials*, 123, 15-26.
38. Sahoo, S.K.; Mohanty, S.; and Nayak, S.K. (2015). Study of thermal stability and thermo-mechanical behavior of functionalized soybean oil modified toughened epoxy/organo clay nanocomposite. *Progress in Organic Coatings*, 88, 263-271.
39. Johnson, R.D.J.; Arumugaprabu, V.; Rajasekar, E.; Santhosh, G.; and Saravanakumar, M. (2018). Mechanical property studies on environmental friendly bio epoxy resin. *Materials Today: Proceedings*, 5(2), 6815-6820.