

Research Article

Investigation of the Impact of Two Types of Epoxidized Vietnam Rubber Seed Oils on the Properties of Polylactic Acid

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To minimize the brittleness of polylactic acid (PLA), the epoxidized rubber seed oils (ERO) or epoxidized ester rubber seed oils (EERO) are blended with PLA. The mechanical properties of ERO bioblend are higher than that of EERO bioblend and significantly improved compared to that of the PLA sample. Elongation at break is increased by 9.1 times, and impact strength and tensile toughness improved by 139% and 1370%, respectively. The morphological study showed the microdroplets of epoxidized oils distributed in the ERO bioblend are much smaller than those in the EERO bioblend. This means that the ERO is better compatible with PLA, and both ERO and EERO are partially miscible with PLA. This compatibility is confirmed by the decrease in the glass transition temperature, T_g , from 65.7 to 60.5°C. The TGA analysis shows a sharp increase in an initial decomposition temperature (from 261.8 to 311.9°C) meaning an improvement in thermal properties. The NMR analysis proves that the epoxidized vegetable oils are linked to PLA chains, so both the melt flow index and an acid value of ERO or EERO bioblend decrease while the thermal stability is improved. The NMR peak area of some signals shows that the ERO is more attached to PLA, proving better compatibility of ERO with PLA, resulting in higher mechanical properties of ERO bioblend. The plasticizing effect of plasticizers is not dependent on the oxygen-oxirane content of the epoxidized oil but is strongly influenced by the acid value. Overall results show that both ERO and EERO can be used as a biodegradable, renewable plasticizer to replace petroleum-based plasticizers for PLA. In addition, the successful modification of PLA by using ERO or EERO promotes the use of this polymer as a potential material for researchers working on PLA applications.

1. Introduction

The finite availableness of oil and also the downside of environmental pollution have placed recent specialists within the event of seeking new raw materials for polymer synthesis starting from nonpetroleum as renewable sources [1–4]. Biodegradable polymers that are made from renewable raw materials provide clear benefits for each user and environmental improvement [1, 5]. One of the foremost common biodegradable polymers is aliphatic polyester [6]. However, biodegradation depends not only on polymers, their structure, but also on the decomposition method, for example, hydrolytic or enzymatic, as pointed by Acik when studying the biodegradability of hybrid quaternized soybean oil and poly(L-lactide)-based polymers [7]. Biodegradation depends

also on compositions of biopolymers. Acik [8] showed that as the molar ratio of PCL:SBO increased, the biodegradability of the resulted polymer decreased. Especially, biodegradation is dependent on the types of polymers. For example, biodegradability of composites of aliphatic polyesters poly(ϵ -caprolactone) (PCL), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), polybutylene succinate (PBS), and poly(lactic acid) (PLA) with abaca fibers was evaluated [9]. It shows that in the case of PCL composite, abaca fibers do not clearly affect the weight loss of the material, because PCL itself has relatively high biodegradability, but it causes the acceleration weight loss in case of PHBV and PBS.

Polylactic acid (PLA), a linear aliphatic polyester, can be made up of renewable plant sources, like starch or sugar [6, 10]. PLA is not solely renewable, biodegradable, and

biocompatible however conjointly capable of processing. It has a spread of fine properties, for example, high mechanical strength, transparency, and moderate barrier capability [2, 6, 11–13]. Thus, it has been applied within the production of containers and fibers, additionally as in packaging, medical, and automotive fabrication fields [2, 5, 13, 14]. Despite these fascinating options, the high brittleness, low toughness, low elongation at break, and low thermal stability of PLA restricted its application [3–5, 14]. Several approaches are taken to boost these properties where the PLA blended or copolymerized with different materials is an associate example [2, 6, 13]. These materials can be non-biodegradable polymers as poly(ethylene oxide), poly(vinyl acetate), and acrylonitrile/butadiene/styrene copolymer [6, 15] or biodegradable polymers as poly(ethylene glycol), poly(vinyl alcohol), poly(caprolactone), poly(hydroxyalkanoate), poly(butylene succinate), and poly(hexamethylene succinate) [2, 5, 6, 13, 15]. Low molecular weight compounds like esters or oligomeric lactic acid, glycerol or triacetate, citrate esters, and epoxidized soybean oil have been used as plasticizers for PLA [6, 13, 16, 17].

The choice of the polymers or plasticizers used to improve the properties of the PLA depends on the requirements of the application. An important demand for a low molecular weight plasticizer is that it should be miscible with PLA to create a homogeneous blend [13]. It is necessary to use renewable plasticizers to effectively improve the properties of the PLA while not sacrificing their biodegradability [6]. These plasticizers should have functional groups like ester or epoxy which are more likely degraded by microorganisms [18]. Recently, epoxidized vegetable oils have gained a lot of interest as a renewable source of plasticizers for polymers because they satisfy requirements such as low volatility, cheapness, good lubricity, high viscosity index, and good solvency for fluid additives [13, 19].

There has been a number of articles dealing with the use of epoxidized soybean oil [2, 6, 15–17, 20], epoxidized palm oil [3, 5, 15], and, most recently, the epoxidized rubber seed oil [14] as plasticizers for PLA. In the case of epoxidized rubber seed oil served as a plasticizer for PLA, dichloromethane was used as a solvent. In the present study, two types of epoxidized rubber seed oil were used as plasticizers for PLA via melt blending technique. The objective of this work is to study the effects of two types of plasticizers based on rubber seed oil on the mechanical and thermal properties, melt flow index, and an acid value of plasticized PLA; the interaction between PLA and plasticizers was also investigated.

2. Materials and Methods

2.1. Materials. The extrusion grade PLA RJ 4210 was purchased from Fisino®. Sodium tungstate dihydrate was purchased from Merck, Germany. Phosphoric acid (85 wt.%), methanol, and hydrogen peroxide (30 wt.%) were obtained from Xilong Chemical, China. Benzyl dimethyl stearyl ammonium chloride was purchased from Tokyo Chemical Industry Co., Ltd. Rubber seeds were collected in Long Khanh, Dong Nai, Vietnam. After 3 months of drying, they were pressed in EC company in 364/1 Cong Hoa, Tan Binh,

to get rubber seed oil (RSO) with an iodine value of 146.9 cgI_2/g and an acid value of 39.03 mgKOH/g . The RSO without further purification was epoxidized by using a sodium tungstate dihydrate catalyst to give a product named ERO. The other way, RSO was firstly modified with methanol to reduce the acid value to 1.12 mgKOH/g , then was epoxidized to the product under the name EERO. The epoxidation reactions were carried out at a temperature of 60°C, for one hour with the molar ratio of double bond/hydroperoxide/sodium tungstate of 1/2/6.5.10⁻³ and sodium tungstate/benzyl dimethyl stearyl ammonium chloride/phosphoric acid of 1/0.25/3 for the ERO case and of 1/0.55/3 for the EERO case. Some characteristics of epoxidized rubber seed oils are shown in Table 1.

3. Methods

3.1. Sample Preparation. The name of samples based on PLA with or without 5 wt.% epoxidized rubber seed oils is given in Table 2. Before commixture, the neat PLA was dried under vacuum at 80°C for four hours whereas the epoxidized oil held on at room temperature. The mixture was introduced step by step to a Brabender mixer. The blending was done at 165°C for five minutes to provide bioblend. PLA sample conjointly underwent melting in Brabender almost like bioblend samples. The samples were ironed at 175°C under the vacuum at 130 kgf/cm^2 to induce the bars of 3 × 10 × 100 mm^3 dimensions or the thin films of the 500 μm thickness on the average. A manual mechanical press was used for manufacturing dumbbell tensile specimens from the films.

3.2. Characterization Techniques. The tensile and impact strengths of samples were determined according to ASTM D638 and D4812 standards, respectively. The morphology of samples was studied by a scanning electron microscope (SEM, JSM-6360/6360LV Japan). The thermal behaviour of the samples was investigated by differential scanning calorimetry (Setaram DSC 131) and thermogravimetric analysis (TGA, Labsys Evo S60/58988, France). The melt flow index of materials ($\text{g}/10 \text{ min}$ at 190°C/2.16 kg) was determined by using the Tinius Olsen device, USA. The acid value of samples was determined according to ISO 2114 standard. The oxirane oxygen content and iodine value of epoxidized rubber seed oils were determined according to AOCS Cd 9-57 and ISO 3961:2018(E) standards, respectively. The nuclear magnetic resonance spectra were recorded on Bruker Avance 500, USA. The solvent used for H-NMR analysis is CDCl_3 . Samples used for HNMR analysis are prepared as follows: dissolve the bioblend sample in CH_2Cl_2 . In this case, PLA, epoxidized oil attached to PLA chains and epoxidized oil not attached to PLA chains dissolved well in the solvent. Precipitating this solution in CH_3OH , the “free epoxidized oil” (not attached to PLA) is not precipitated, because it dissolves well in CH_3OH , so it will remove non-PLA-attached epoxidized oil. The purification is repeated 5 times to ensure that the “free epoxidized oil” is completely removed.

TABLE 1: Some characteristics of epoxidized rubber seed oils.

Properties	ERO	EERO
Oxygen-oxirane content (%)	6.3	7.5
Acid value (mgKOH/g)	9.33	0.75
Iodine value (cgI ₂ /g)	12.24	12.69

TABLE 2: The names of bioblend and its composition.

Samples	PLA (wt.%)	ERO (wt.%)	EERO (wt.%)
PLA	100	0	0
ERO bioblend	95	5	0
EERO bioblend	95	0	5

4. Results and Discussion

4.1. Mechanical Properties. Tensile properties are the most frequently used as an indicator of plasticization effectiveness. As can be seen from Figure 1, the stress reduced with the presence of epoxidized rubber seed oils whereas the strain grew up powerfully. The tensile of the ERO and EERO bioblends was not much different; however, the strain of ERO bioblend was a lot larger than that of EERO one. The elongation at break, tensile, and modulus of samples with and without modified rubber seed oils is given in Figure 2. The presence of epoxidized rubber seed oils reduced the tensile of the material from 52.31 MPa (PLA) to 41 MPa (ERO bioblend) and to 35.39 MPa (EERO bioblend). So, it exhibited a reduction in tensile strength of 21.6 and 32.3% over the sample without epoxidized rubber seed oil (see Figure 2). It is understandable that the reduction of tensile is related to the formation of epoxidized rubber seed oil domain within the PLA matrix.

As can be seen from Figure 1, the slope of stress-strain curves in the elastic deformation region of the three tested samples was nearly similar, so their tensile modulus was not much different. That means, the tensile modulus was not much influenced by adding epoxidized rubber seed oils, so the stiffness of PLA product did not much change in the presence of epoxidized rubber seed oil (see Figure 2).

The presence of ERO or EERO plasticizers did not considerably have an effect on the module, whereas it had a strong impact on strain (see Figure 1) and elongation at break (see Figure 2). Though PLA has the advantage of biodegradability and renewable sources, it has a limitation of being terribly brittle; for instance, the elongation at break of PLA was terribly little (6.23%).

The presence of EERO plasticizer in EERO bioblend brought in 2.6 times increases in elongation at break. Specifically, the elongation at break of PLA enlarged up to 9.1 times when using ERO as a plasticizer (see Figure 2). That means, the ERO had a better plasticizing impact than EERO. Indeed, the presence of ERO or EERO plasticizers reduces the intermolecular force. The space between the molecules is widened; the molecules easily slide relative to each other and so will increase the PLA's flexibility [21]. This result was similar

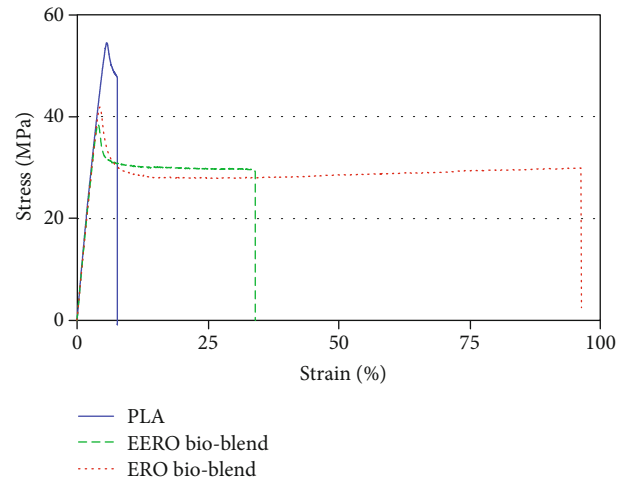


FIGURE 1: The relationship between stress and strain.

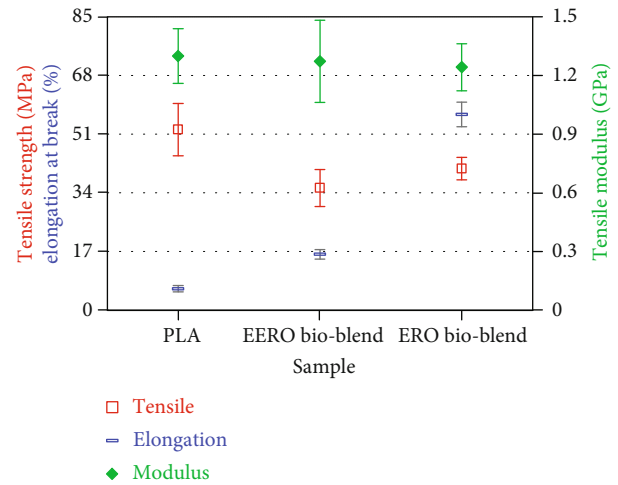


FIGURE 2: The effect of modified rubber seed oils on tensile properties.

to that of Tee et al.'s work when using epoxidized palm oil to plasticize PLA [22].

It has been reported that the plasticizing impact of epoxidized vegetable oils on PLA was due to the interaction between the hydroxyl groups that belong to carboxyl groups in PLA and the epoxy groups of epoxidized vegetable oils [3, 4, 20]. Due to the polarity of C-O bonds, the electron-deficient carbon of oxirane constitutes an active site for nucleophilic reactions. However, the oxirane groups in epoxidized vegetable oils lay on the backbone, so they are hindered at both carbons and electron-donating alkyl substituents. Therefore, their activity is less than that of the terminal epoxy group [23]. On the other hand, since the OH group in PLA is a weak nucleophile, therefore, the epoxy ring-opening reaction takes place with the SN1 substitution mechanism, meaning the epoxy should first be protonated before nucleophile attacks on carbon; thus, the reaction between the epoxy group and the hydroxyl group is catalyzed by acid. On the other hand, compared to EERO, ERO has a

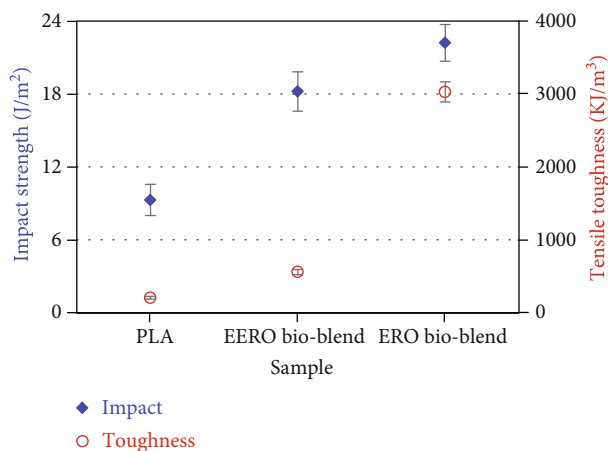


FIGURE 3: The effect of plasticizers on impact strength and tensile toughness.

higher acid value, so it is potential that the epoxy group of it will react well with the OH group of PLA leading to a better plasticizing impact as compared with EERO. This interesting issue will be further investigated by nuclear magnetic resonance analysis.

PLA is known for its high brittleness, and the impact strength of PLA is only 9.28 J/m^2 (see Figure 3). It can be noticed from Figure 3 that the presence of epoxidized rubber seed oil plasticizers in the PLA matrix resulted in a drastic increase in impact strength. Like the case of elongation at break, in the presence of EERO plasticizer, the impact strength was improved by 96%, whereas the presence of ERO was improved by up to 139% compared to the impact of PLA.

As can be seen from Figure 1, with the presence of ERO and EERO, the tensile of the bioblend decreased whereas the elongation at break increased greatly; especially, it grew up remarkably in the case of ERO bioblend. The tensile toughness of samples was obtained by calculating the area under the stress-strain curves of the tensile test. The result is introduced in Figure 3. The plasticizing effect of epoxidized rubber seed oils was clearly shown not only by a significant improvement in elongation at break or impact strength but also by a sharp increase in tensile toughness (see Figure 3). The key to good toughness may well be a combination of strength with ductility. The tensile strength of PLA was the highest; however, the elongation at break of it absolutely was very low, leading to the lowest tensile toughness. The tensile strength of EERO bioblend was 32% lower, but elongation at break of it was 2.6 times higher than that of PLA (see Figure 2); therefore, the tensile toughness of EERO bioblend was 171% higher (see Figure 3). The elongation at break of ERO bioblend was the best and 9.1 times more than that of PLA (see Figure 2), leading to the best tensile toughness (see Figure 3). The tensile toughness of ERO bioblend was 3029 KJ/m^3 , 442% more than that of EERO bioblend, and 1370% more than that of PLA (see Figure 3). That means the plasticizing impact of ERO epoxidized rubber seed oil was more than that of EERO. Similar to the case of elongation at break, the higher plasticizing impact of ERO is believed because of the reaction of the OH and/or COOH

groups of PLA with the epoxy group of ERO, which is effectively catalyzed by its higher acidity.

4.2. Morphology. A sharp increase in elongation at break and tensile toughness of the studied materials showed the transition from the brittleness of PLA to the ductility of bioblends. The efficiency of plasticization is strongly dependent on the compatibility of the plasticizer and PLA. The miscibility may be inferred from the solubility parameters of the two components that are blended. The compatibility of plasticizer requires a similarity in solubility parameters between plasticizer and polymer [1, 13, 24].

The Hildebrand solubility parameter is defined as the square root of the cohesive energy density [25, 26] and the cohesive energy and molar volume of the molecules may be predicted by means of additive functions [25]. Therefore, the solubility parameters of PLA, ERO, and EERO were 22.75, 21.75, and 19.22 $\text{MPa}^{0.5}$, respectively, when using Fedors cohesive energy (E_{coh}) and molar volume (V) [25]. These values were not similar but close to each other that indicated ERO and EERO should be partially miscible with PLA [6, 26, 27]. Thus, ERO and EERO may form a second dispersed phase when they were blended with PLA. This dispersed phase would form many microdroplets dispersed evenly in the PLA matrix. The morphological structure of the impact fractured surface of bioblends was very well demonstrated by microvoids shown in Figure 4.

The solubility parameter of ERO was nearer to PLA than that of EERO; thus, ERO would be better compatible with PLA, leading to smaller microvoids in the second dispersed phase of ERO bioblend (see Figure 4(b)) as compared therewith of EERO bioblend (see Figure 4(c)). On the other hand, as per the reports in previous studies [6, 15], the PLA is extremely brittle as a result of the failure that happens by microcracks spreading easily and freely. The second dispersed phase of ERO or EERO could have an associate influence on the crack propagation in bioblends. The microvoids dissipate a large part of the fracture energy throughout the crack bifurcation, delay, or stop the expansion of cracks and alter the crack path, creating by this way the cracks not to spread freely [6, 15]. This can be the explanation for the rise in tensile toughness and impact strength once ERO or EERO was added to PLA.

4.3. Thermal Properties. Differential scanning calorimetry (DSC) measures the amount of heat released or absorbed once the material is cooled or heated. The DSC thermograms from -50 to 300°C of samples are demonstrated in Figure 5, and the characteristics of thermal behaviour are summarized in Table 3.

The curves of samples exhibited three thermal transitions, i.e., glass transition (T_g), cold crystallization (T_c), and melting (T_m) temperatures (see Figure 5). PLA showed T_g , T_c , and T_m peaks located at 67.6°C , 115.5°C , and 167.5°C , respectively. The epoxidized rubber seed oils brought the decrease in glass transition temperature from 65.7°C to 63.3°C by adding ERO and 60.5°C by adding EERO, indicating that both ERO and EERO were partially miscible with PLA.

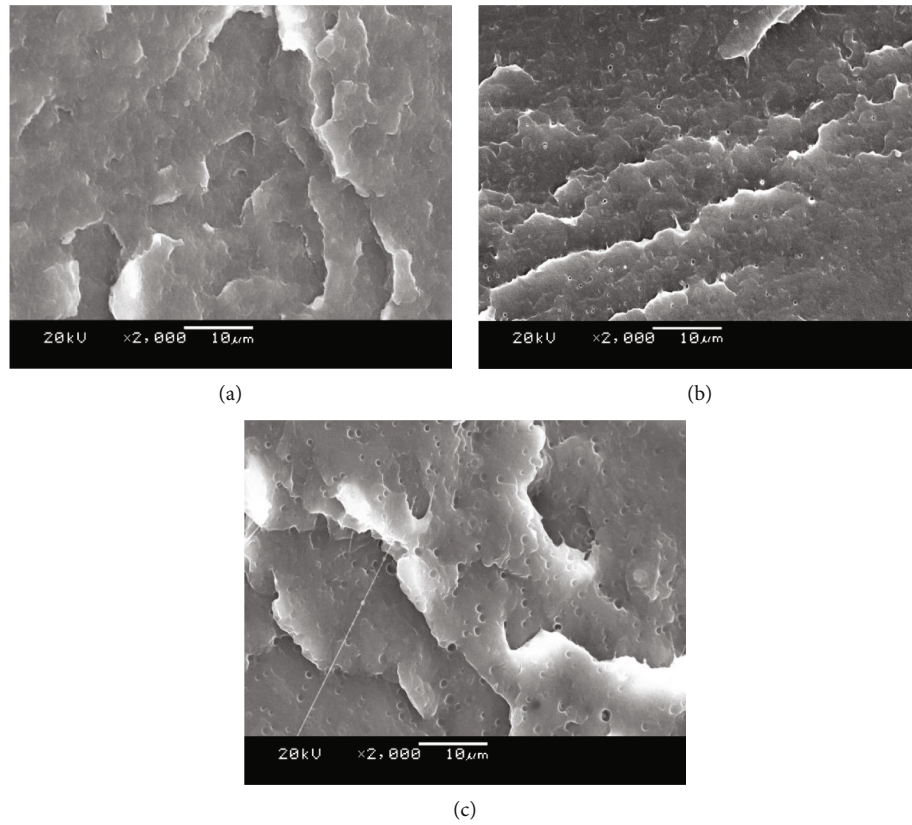


FIGURE 4: SEM of PLA (a), ERO bioblend (b), and EERO bioblend (c).

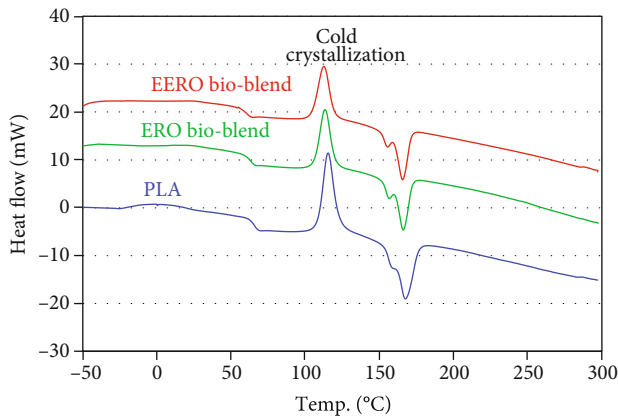


FIGURE 5: DSC thermograms of samples.

TABLE 3: The characteristics of thermal properties.

Samples	T_g (°C)	T_c (°C)	T_m (°C)	χ_c (%)
PLA	65,7	115,5	167,5	3,00
ERO bioblend	63,3	113,4	166,0	1,28
EERO bioblend	60,5	112,5	165,8	1,48

An endothermic peak of melting of ERO and EERO bio-blends was 166.0 and 165.8°C, respectively. A minor decrease in the melting temperature by 1.5 to 1.7°C was observed,

indicating that the melting temperature of PLA was not greatly affected by the addition of modified rubber seed oil plasticizers (see Table 3). Furthermore, the cold crystallization temperature of PLA reduced by the introduction of ERO or EERO (see Figure 5), which suggests that the ability to cold crystallization of PLA was increased by them. It is clear that the T_c of PLA decreased in parallel with the shift in T_g . A reduction of T_g and enhancement of the cold crystallization process are due to the increase in segment mobility of the PLA chains thanks to plasticization and are often observed for plasticized PLA systems [17].

The crystallinity of the sample was calculated per the enthalpy obtained from the DSC curves. The proportion of crystal, χ_c , was calculated by using the subsequent equation:

$$\chi_c(\%) = \frac{|\Delta H_m - \Delta H_c|}{|\Delta H_m(100\%)|} \times 100\%. \quad (1)$$

Here, ΔH_c is the enthalpy of crystallization (J/g), ΔH_m is the enthalpy of melting (J/g), and $\Delta H_m(100\%)$ is the enthalpy of melting (93 J/g) of PLA with a crystallinity of 100%. In this experiment, the χ_c of PLA was 3% and the degree of crystallization decreased when ERO or EERO was added. ERO and EERO bioblends with the crystallinity of 1.28% to 1.48% were almost amorphous.

Thermogravimetric analysis (TGA) was used to study the thermal stability of samples as a result of it providing information on the weight loss thanks to degradation as a function

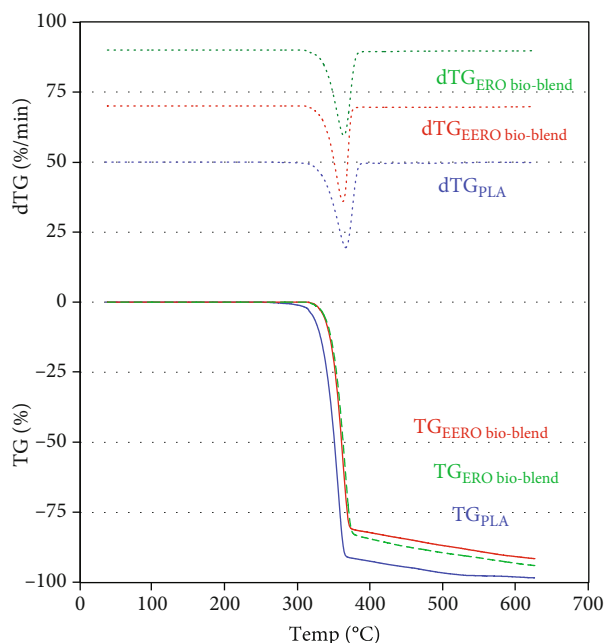


FIGURE 6: TG and dTG thermograms of samples.

TABLE 4: The thermal stability factors of samples.

Sample	T_{onset} (°C)	T_{max} (°C)	% weight loss at 384°C
PLA	261.8	362.9	91.2
EERO bioblend	308.8	361.7	81.5
ERO bioblend	311.9	363.8	83.5

of temperature. Besides the weight loss, associate initial decomposition temperature (T_{onset}) and the temperature of a maximum rate of degradation (T_{max}) were conjointly the thermal stability factors. Figure 6 represents the weight loss curves (TG) and the corresponding first derivative curves (dTG) of samples.

It can be seen that the thermal decomposition behaviour of all samples is sort of equivalent as a result of it taking place in just one step; the dTG curve encompasses a single peak. The decomposition temperature commenced near to 300°C and continued till 380°C (see Figure 6). However, the T_{onset} and the weight loss at 384°C of samples were quite different. The T_{onset} of PLA was 261.8°C, lower by 47.0 to 50.1°C compared thereupon of EERO or ERO bioblends. The weight loss of PLA at 384°C was 91.2% whereas it was 83.5% and 81.5% for ERO and EERO bioblend, respectively. That means the thermal stability of the materials was considerably improved by the presence of epoxidized rubber seed oils dispersed in the PLA matrix. It is the dispersion state that makes a protective physical barrier on the PLA surface to prevent the permeability of volatile degradation products from the PLA plasticized by the epoxidized rubber seed oil and, finally, helps delay the degradation of ERO or EERO bioblends [3, 28]. The presence of epoxidized rubber seed oils has greatly affected the T_{onset} and the weight loss, however not much impact on the T_{max} (see Table 4). Using epoxidized vegetable oil to plasticize

PLA often improves thermal stability [3, 4, 22]; the epoxidized rubber seed oils in our case also have the same effect.

4.4. Melt Flow Index (MFI) and Acid Value. After undergoing the healing process, both the MFI and acid value of the PLA sample were higher than those of neat PLA (with no thermal treatment). The increase in MFI indicated that the molecular size of the PLA sample became smaller because of breaking PLA chains by the melting mixing process. The broken PLA chains caused an increase in the ends of chains, as well as in the COOH group content, resulting in an increase in the acid value (see Table 5).

Figure 6 and Table 4 show that the presence of ERO or EERO improved the thermal stability of plasticized PLA thus minimizing thermal decomposition during the melting mixing process, resulting in lower acid value and MFI of ERO and EERO bioblends than PLA sample. However, the results in Table 5 show that both acid value and MFI of ERO and EERO bioblends were much smaller than that of not only the PLA sample but also the neat PLA. The sharp decrease of those characteristics may be due to the -OH and -COOH inherent groups in PLA and the newly formed groups by the thermal decomposition of PLA react with epoxy groups of epoxidized rubber seed oil, creating a rise in molecular size and reduction in acid group content and leading to lower acid value and MFI of ERO and EERO bioblends as compared with both PLA sample and neat PLA.

Due to the fact that the reaction between the epoxy group and the weak nucleophile agents is catalyzed with acid, along with the fact that the acid value of ERO is greater than that of EERO, the reaction between the epoxy groups of ERO and the OH or COOH groups of PLA will be more easily (compared with the reaction between an epoxy groups of EERO and OH or COOH groups of PLA). This is the reason why both the acid value and the MFI of ERO bioblend are smaller than those of EERO bioblend (see Table 5). Evidence for these reactions will be found in the NMR spectrum (see Figure 7).

4.5. Nuclear Magnetic Resonance. Figure 7 shows proton NMR spectra of PLA, ERO, and EERO bioblends. The diagnostic signals of protons are listed in Table 6. It can be seen that the signal of methine proton at 5.1 ÷ 5.2 ppm, methyl proton of repeat units at 1.5 ÷ 1.6 ppm, and proton of terminal methyl adjacent to C that links to OH-group at 1.4 ÷ 1.5 ppm were observed in PLA and both bioblends. The signal “d” at 1.2-1.3 ppm may be related to the proton of the CH₃ group in the isopropyl group of the initiator connected to some PLA chains [29]. However, the area of peak “d” in PLA is only 0.01. On the other hand, the signal at 1.2-1.3 ppm, “m” also characterizes protons of many CH₂ groups in epoxidized oil. This signal in ERO or EERO bioblends has a peak area much larger than that of the PLA, indicating the contribution of both proton “d” and “m” to the signal. It should be noted that the “free” epoxidized oils after 5 purification times have been removed, so the signal at 1.2-1.3 ppm of the CH₂ proton belongs to the epoxidized oils chemically connecting with the PLA. But even in the case if the “free” epoxidized oil remains in the PLA matrix after purification,

TABLE 5: The MFI and acid value of neat PLA and samples.

Properties	Neat PLA	PLA	Samples ERO bioblend	EERO bioblend
MFI (190°C, 2.16 kg) (g/10 min)	8.50	11.16	5.11	6.84
Acid value (mgKOH/g)	1.84	2.00	0.89	0.92

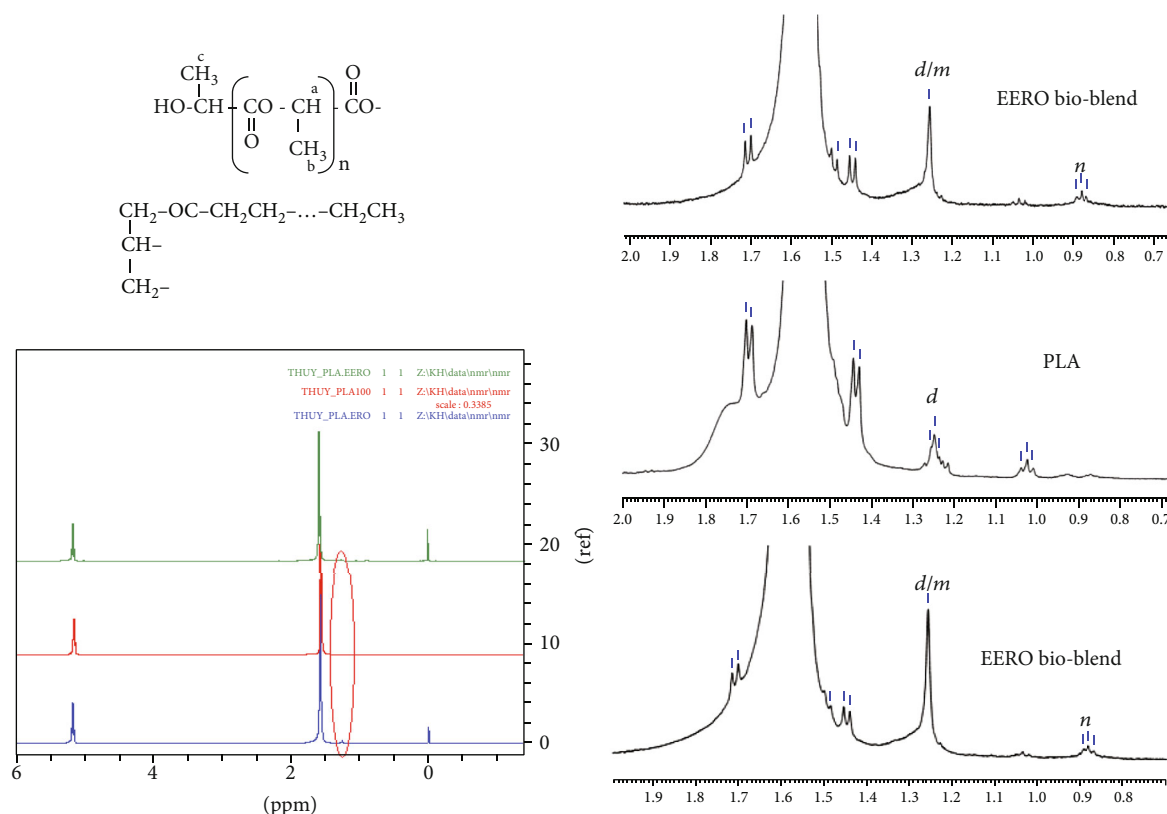


FIGURE 7: The H-NMR spectra of samples.

TABLE 6: Assignment of the H-NMR spectra of samples.

Signal	ppm	PLA	Area EERO bioblend	ERO bioblend
a—CH (repeat units)	5.1 ÷ 5.2	1	1	1
b—CH ₃ (repeat units)	1.5 ÷ 1.6	3.03	3.9	3.57
c—CH ₃ (terminal)	1.4 ÷ 1.5	0.03	0.07	0.05
d/m	1.2 ÷ 1.3	0.01	0.09	0.12
n	0.8 ÷ 0.9	0	0.02	0.02

it should coexist with the epoxidized oil that linked to the PLA. Because only the latter oil can reduce the acid value and melt flow index of the blend compared to those of PLA and neat PLA (see Table 5).

Furthermore, the signals “n” at $0.8 \div 0.9$ ppm related to the proton of the $-CH_3$ terminal group in the epoxidized oil

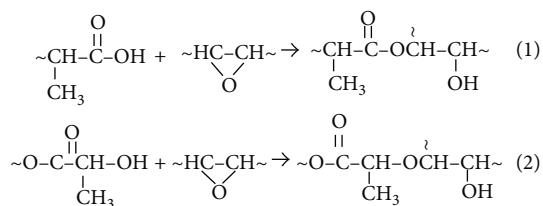


FIGURE 8: Reactions between epoxy groups of epoxidized oil and carboxyl (2) or hydroxyl (3) end of PLA chains.

that not seen in spectrum of PLA but appeared in spectra of ERO and EERO bioblends. So, the information of signal at $1.2 \div 1.3$ ppm and $0.8 \div 0.9$ ppm finally proved that the epoxidized rubber seed oils were attached to the PLA chains. This means a chemical reaction between the epoxidized rubber seed oils and PLA occurred. These reactions could be (2) and/or (3) shown in Figure 8. Thanks to these reactions, both the MFI and acid value of ERO and EERO bioblends were smaller than those of the PLA samples and even smaller than those of the neat PLA.

Table 6 also shows that the peak area at $1.2 \div 1.3$ ppm of ERO bioblend was larger than that of EERO bioblend, which suggests that the number of $-\text{CH}_2$ groups of ERO appeared more in PLA chains. This proves that the OH and COOH groups of PLA more easily react with the epoxy groups of ERO than of EERO, so both the MFI and the acid value of ERO bioblend were less than those of EERO bioblend. This could be the explanation of why the mechanical properties of PLA in the presence of ERO are improved better than in the presence of EERO.

5. Conclusions

The presence of both epoxidized-rubber seed oils considerably improved the mechanical properties of PLA. Especially, ERO has a more positive effect in reducing the brittleness of the PLA. This has been clearly demonstrated by increasing the elongation at break, impact strength, and tensile toughness. The morphological structure of the impact fractured surface also showed that the ERO was more compatible with PLA. This better miscibility was not only due to the ERO's solubility parameter being closer to that of PLA but also because the ERO was more attached to the PLA chains. This result was proved by the peak area of some signals on the HNMR spectrum. The fact that ERO is better compatible with PLA than EERO resulting in both the melt flow index and the acid value of the ERO bioblend being smaller than those of the EERO bioblend. The plasticizing effect of the studied plasticizers is independent of the oxygen-oxirane content of the epoxidized oil but is powerfully influenced by their acid value. Overall results show that both ERO and EERO can be used as a biodegradable, renewable plasticizer to replace petroleum-based plasticizers for PLA. In addition, the successful modification of PLA by using ERO or EERO promotes the use of this polymer as a potential material for researchers working on PLA applications.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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