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Epoxidized Olive Oil as a Sustainable Plasticizer to Polylactic Acid

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Abstract
The consumption of synthetic, non-biodegradable polymer plastics has drawn attention to growing environmental concerns, prompting the development of other materials, particularly bio-based materials. Biopolymer-based biocomposite materials are plasticized to improve their ductility. In this study, five distinct weight ratios of biopolymers (PA/EOO), 90 wt.%, 80 wt.%, 70 wt.%, 60 wt.%, and 50 wt.% were employed as plasticizers for poly-lactic acid (PA) in a fluid molding process. The mechanical, thermal stability, and morphological characteristics of the blends were each examined using a viscometer measurement (R.V.), tensile properties (TP), a scanning electron microscope (SEM), and a thermogravimetric analyzer (TGA). All composite materials (PA/EOO) mixtures show notable improvements in mechanical properties and excellent thermal stability when compared to pure PA. The maximum PA/EOO elongation at break was around 213 % when the PA/EOO mix was 80 wt %. Attractive morphological results from composite materials (PA/EOO) blends showed that EOO was compatible with PA and that the resulting composite material (PA/EOO) was thought to be an ecologically beneficial mixture because it contained vegetable oil.

Keywords: biopolymers, plasticizer, olive oil, polylactic acid, composite materials

أيبوكسيد زيت الزيتون كمادة ملدنة مستدامة لمتعدد حامض اللبنيك

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الخلاصة
مواد مركبة متمثلة بالبوليمرات الحيوية تم تدلينها لتحسين الليونة ، في هذه الدراسة حيث تم استخدام أيبوكسي زيت الزيتون (EOO) كمادة ملدنة لحامض اللبنيك (PA) بطريقة صب السوائل باستخدام الكلوروفورم كمذيب عند خمسة نسب وزنية مختلفة للبوليمرات الحيوية (PA / EOO) 90٪ وزنا ، 80٪ وزنا ، 70٪ وزنا ، 60٪ وزنا ، 50٪ وزنا. تم استخدام قياس مقياس اللزوجة (R.V.) ، وخصائص الشد (TP) ، والماسح المجهري الألكتروني (SEM) ، ومحلل قياس الوزن الحراري (TGA) لفحص الثبات الميكانيكي والحراري والخصائص المورفولوجية للخلطات ، على التوالي. بالمقارنة مع PA النقي ، تُظهر جميع نسب خلطات المواد المركبة (PA / EOO) تحسينات كبيرة في الصفات الميكانيكية وأستقرار حراري كبير . عندما كان مزيج 80

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٪ (PA / EOO) وزنا ، حصلنا على أقصى استطالة عند الكسر حوالي 213٪. أسفرت خلطات المواد المركبة
(PA / EOO) عن نتائج مورفولوجية جيدة ، مما يشير إلى أن EOO كان متوافقًا مع PA وكذلك المادة المركبة
(PA / EOO) الناتجة تعتبر صديقة للبيئة بسبب استخدامها للزيت النباتي .

1. Introduction

Due to their biodegradability and biocompatibility, which offer obvious advantages to both consumers and the environment, bio-degradable poly-esters have attracted a lot of attention.

As a structural material, PA is a viable technological substitute for petrochemical polymers since it is biodegradable and developed using renewable resources [1, 2].
Because of its mechanical attributes and processing versatility, poly-lactic acid is an excellent choice for manufacturing disposable packaging [3]. PA is used in the pharmaceutical, automotive, and textile industries. However, its strong tensile, strong modulus, low elongation at break, and high price limit its use. Its features must be modified to satisfy end users' demands [4, 5].

In order to increase flexibility and other mechanical qualities, poly-lactic acid has been mixed with other polymers [6-9]. To improve the TP of PA, plasticizers including polyethylene glycol have also been utilized [10-13].

Epoxidized olive oil (EOO) is a combination of various fatty acids in glycerol esters that have undergone epoxidation. As the raw ingredients are renewable, biodegradable, ecologically friendly, and widely accessible, many chemical firms rely on them.

Epoxidized oil's limited compatibility with polymers and the oil's inherent low iodine value are two limitations that prevent EOO from being widely used as a plasticizer. Instead, are frequently employed as plasticizers. According to Ali et al. (2009) and Gan et al. (1995) [14, 15], epoxidized soy oil was employed as a plasticizer to increase the flexibility of PA. Thermal and SEM analysis led them to the conclusion that epoxidized soy oil is moderately miscible with PA following heat treatment. They discovered that after heat treatment, epoxidized soy oil is somewhat miscible with PA after thermal and SEM investigation. Rheological and mechanical properties may be found in biopolymers (PA/Epoxidized soy oil) mixtures. Epoxidized soybean oil now has better melt properties and rheological extension upon rupture [16].

The purpose of this investigation was to examine the effects of epoxidized olive oil (EOO) on the thermal-stability, tensile characteristics, and morphological qualities of PA as well as the interaction of PA and EOO in composite materials (PA/EOO blends). This has been accomplished by using a casting solution technique with chloroform as the solvent.

2. Experimental

2.1. Materials

The EOO was given by Malaysia's Advanced Oleo-chemical Tech. Division (AOTD). PA with chloroform was obtained from Nagoya, Japan through local sources.

2.2. Preparation of polymers (PA/EOO) blends

The appropriate concentrations of PA and EOO were dissolved in 50 mL of chloroform. The EOO was lowered into the PA and blended steadily. After adding the EOO solution to the PA, the resultant mixture was stirred for an hour. It was then refluxed for two hours. In a Petri plate, the PA/EOO mixture was poured and allowed to dry. Table 1 shows the ratio of PA to EOO employed in this investigation.

Table 1: Percentage of PA/ECC blends

Identification of the sample	PA (g)	EOO (g)
Pure PA	10.0	0.0
90 wt.% PA	9.00	1.00
80 wt.% PA	8.00	2.00
70 wt.% PA	7.00	3.00
60 wt.% PA	6.00	4.00
50 wt.% PA	5.00	5.00

2.3. Viscometer measurement (R.V.)

A viscometer of the type Ubbelohde (ASTM) was used to measure viscosity. The lowered viscosity values (R.V.) were determined and plotted against the concentration of PA/EOO using Huggin's Eq. (1) [17].

$$R.V = (T - T_{\circ})/(T_{\circ}.C) \qquad (1)$$

where T = PA/EOO mixing time, hr.; T_o = purified solvent time, hr. and C is the PA/EOO mixing solution concentration (mol./L).

2.4. Tensile properties (TP)

According to ASTM D638 [18], the tensile characteristics are determined at break using an IUTM 4301 with a crosshead speed of 5 mm/min. In the tensile test, six samples were utilized, and the final result was calculated using the average of five results.

2.5. Scanning electron microscope (SEM)

The microstructure of the blend's tensile brittle failure at room temperature was examined using a scanning electron microscope. A JEOL SEM (type JSM-6300F) with an energy dispersive discharge and a 5 kV power was used. A thin layer of gold with a width of a few nm was applied to surfaces that had undergone tensile fracture.

2.6. Thermogravimetric analysis (TGA)

The thermal stability of the samples has been examined using the TGA (Type, CMT4503, MTS Inc., China). A TGA was used to calculate the specimens' weight loss. The specimens were in a nitrogen environment with a fluid velocity of 20 mL/min and a temperature range of 10 ˚C/min from 30 to 800 ˚C.

3. Results and discussion

Reduced viscosity of PA/EOO mixes in solution as a function of concentration and demonstrates the impact of EOO on PA viscosity was studied at room temperature as shown in Figure 1. It can be seen that increasing the amount of EOO in the PA/EOO mixture causes the viscosity to decrease in all sets of PA/EOO mixes. The figure also demonstrates lowered viscosity as the concentration increases. Increasing the concentration leads to a change in the properties increasing the flexibility of the polymer due to fluidity of the mix.

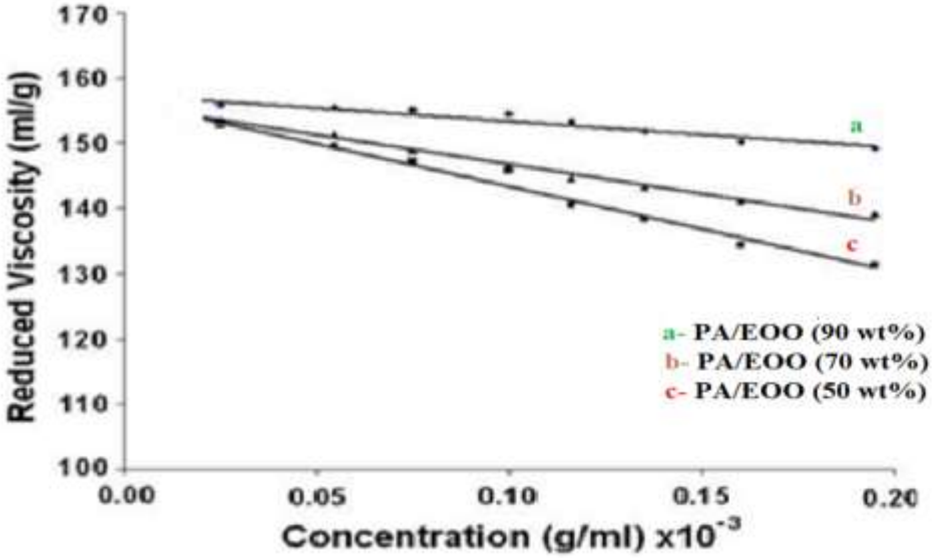

Figure 1: Reduced viscosity of PA/EOO mixes in the solution as a function of concentration.

Tensile tests performed at room temperature on a universal testing machine (CMT4503, MTS Inc., China) were utilized to examine the mechanical characteristics of the PA/EOO composites. According to ASTM D638-03, an inject-molded test specimen was created. According to Figure 2a, a pristine PA sample has a tensile strength of about 25 MPa. The tensile modulus of polyamide PA decreases when plasticizer (EOO) concentrations rise. The valuable tensile strength is lowered by around 70% with the use of 50% softener (Figure 2a).

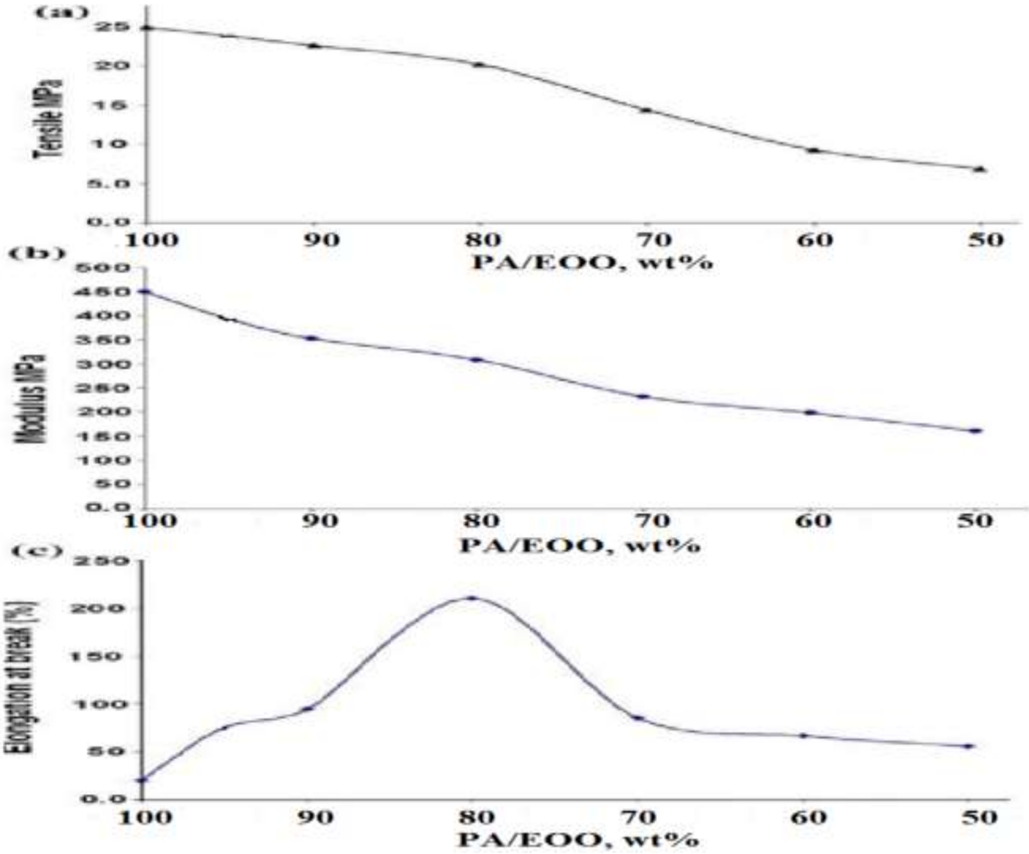

Figure 2: Mechanical properties of PA/EOO mix: (a) Tensile, MPa (b) Modulus, MPa (c) Elongation at break (%).

The gradient of the Wright's modulus curve is often measured to determine stiffness [19]. Figure 2b shows the Young's modulus curves for pure PA and PA/EOO mixes. When EOO is added, the stiffness is significantly decreased and the modulus of neat PA is 450 MPa. A drop in modulus value of 355 MPa was achieved with the addition of 10% EOO. A decrease of 165MPa was obtained by increasing this to 50% EOO.

Figure 2c illustrates the ductility brought on by the presence of EOO. When EOO is added, the ductility of plain PA increases from 30% to 40%. As elongation at break and brittleness are inversely related, the addition of 20% EOO results in the maximum elongation at break (213%), suggesting that the brittleness of the samples reduces. The elongation at break reduces when more EOO is added, making the mixture more brittle. Researchers draw the conclusion that when the proportion of EOO reaches 20%, there is a substantial inclusion of PA with EOO. As the percentage of EOO increases, the characteristics of the mixture become weaker because the inclusion reduces the likelihood of individual agglomerates forming between the mix's components.

The tensile characteristics of insoluble monomer mixtures are known to be influenced by their morphologies [20]. For combination PA and epoxidized soy oil, the relationship between mechanical characteristics and morphology has been reported [14]. In this study SEM was used to examine the interval geometry of the pure PA and PA/EOO blends. Figure 3 shows the SEM images of the PA and PA/EOO blends. SEM micrographs of PA/EOO blends demonstrate very good compatible morphologies, with no edge, hollow, or holes caused by strong interaction. It is conceivable, that the high adherence of these mixes is owing to bonding between PA and EOO, which may result in hydrogen bonds.
Different phase morphology appeared in PA/anhydride soy oil mixtures, with tiny molecular anhydride soy accumulating during stage separation and generating micro-voids in the PA mixture [13].

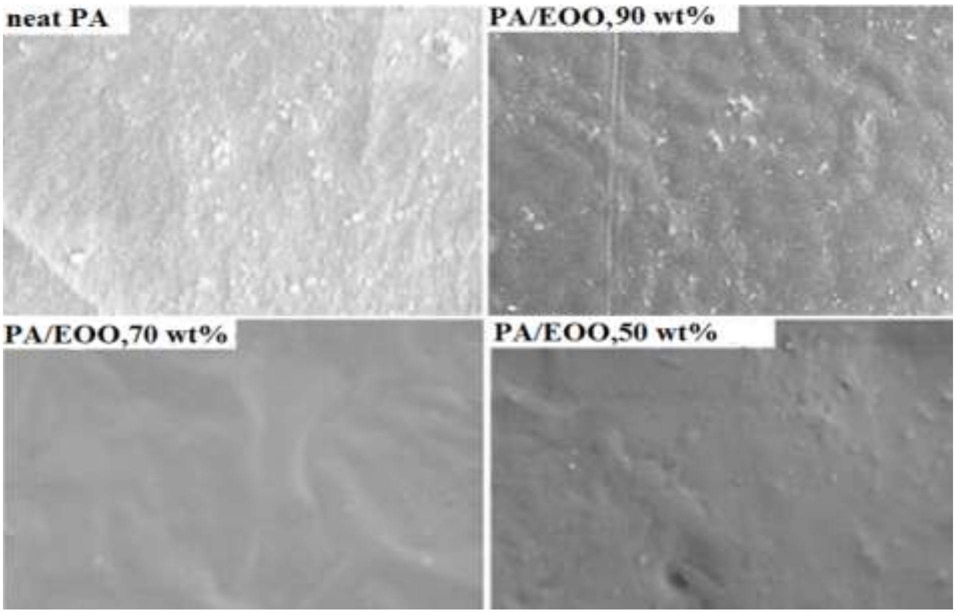

Figure 3: SEM images of PA and PA/EOO blend fracture surfaces.

The heat sensitivity of PA/EOO blends was examined using thermoradimetric analysis. Blends that decompose at a higher temperature offer better thermal stability. The thermochemical breakdown temperature is illustrated in Figure 4. For PA/EOO mixes, the thermal sensitivity of the PA materials was improved with the inclusion of EOO. For instance, for PA increased from 237.45 to 283.42 °C.

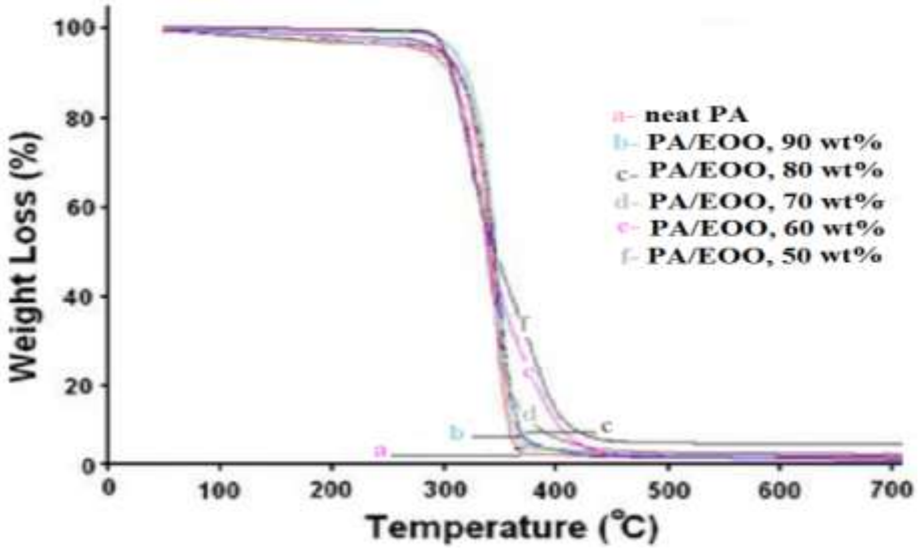

Figure 4: TGA of PA and PA/EOO mixtures

The thermochemical breakdown temperature increased from 371.85 to 457.15 C when the mass factor of EOO was raised to 20%. (Figure 4c). The EOO effect resulted in an improvement in the thermal stability of PA. By decreasing its heat sensitivity, EOO boosted PA's thermal stability by restricting its molecular chain. The behavior of plasticized thermoplastics has been observed in earlier investigations [21-23].

4. Conclusion

This research describes the use of PA along with a new plasticizer (EOO) that used a solution molding process with chloroform as a lubricant. Once the amount of EOO was raised, the mixes' lower viscosities further decreased. The results imply that using EOO could result in more adaptability. The best component of the PA/EOO mixture to improve ductility was discovered to be 20% EOO.

In comparison to pure PA, biopolymers (PA/EOO blends) show noticeably better mechanical and thermal stability properties and will be more ecologically friendly. SEM micrographs reveal that PA and EOO are compatible in the production of composites.

Conflict of Interest:

The authors declare that they have no conflicts of interest

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