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Effect of Epoxidized Waste Cooking Oil Plasticizer in Improving the Mechanical Properties of Polylactic Acid (PLA)

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A synthetic polymer called poly (lactic acid) (PLA) is produced from renewable materials such as starch compounds. PLA is widely used for engineering plastics, food packaging and also for agricultural purposes. The primary disadvantage of PLA in the polymers industry is its brittleness. Because of that, several studies have been performed to enhance mechanical properties through the addition of bio-based plasticizers in polymer compositions. This research work aims to investigate the mechanical properties which is followed the standard method such as flexural strength (ASTM D790), impact energy (ASTM D256) and hardness (ASTM D785). PLA blended with a copolymer bio-based plasticizer, Epoxidized Waste Cooking Oil (EWCO), using the melt blending method via twin screw extruder. The PLA/EWCO blends were prepared using hot press to analyze mechanical properties. The PLA/EWCO blends enhance mechanical properties such as flexural strength, flexural extension and impact energy. Five different blending ratios of PLA/EWCO were examined, 0 %, 2.5 %, 5 %, 7.5 % and 10 % of EWCO in PLA. 2.5 % EWCO demonstrated as the optimum amount to be added, which shown in improvement for both flexural strength and impact energy at 6.738 MPa and 1.45 kJ/m2. From this study, PLA/EWCO demonstrated an alternative solution to replace petroleum-based plasticizers such as phthalate compounds and also resolve the brittleness and enhance all of neat PLA's properties, making it a potential renewable bio-based plasticizer.

1. Introduction

The improper disposal of plastic garbage contributes to environmental problems such as soil, water, and air pollution. The surrounding plastic trash does not organically deteriorate on its own. Plastic takes 50 years or more to completely break down in the soil due to the slow rate of breakdown (Omar et al., 2021). There are three primary categories for the repercussions of improper disposal and mishandling of plastic garbage, involving the damage that it causes to the environment, human health, and sea life (Evode et al., 2021). Degradation of the soil may result from improper plastic trash disposal. Due to its organic decomposition's chemical decomposition, plastic wastes are the ones that contaminate land (Pawar, Shirgaonkar and Patil, 2016). Micro plastics, which are little pieces of plastic that are easily absorbed into the environment through primary and secondary sources, are also present in plastic garbage (Evode et al., 2021).
The burning of plastic trash results in air pollution, which releases poisonous fumes, soot, and solid residual ash which are harmful to human health. Several studies indicate that soot and solid residual ash, particularly volatile organic compounds (VOCs), smoke (Hafidzal et al., 2013), polycyclic hydrocarbon (PAH), and dioxins (Verma et al., 2016) have a significant potential for having a negative impact on one's health and the environment. These particles can travel throughout the environment which ends up in our food chain. These harmful substances deteriorate respiratory conditions including asthma, emphysema, rashes, nausea, or headaches and disrupt the neurological system. They additionally increase the risk of heart disease (João et al., 2020).

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Disposal of plastic waste can cause water pollution where large amounts of plastic seen to forms as litter in the aquatic environments. Plastic debris makes up a significant portion of litter seen in aquatic environments. The biggest contributors to the problem are land-based issues including sewage waste and land-based rubbish (Pawar, Shirgaonkar and Patil, 2016). Several species, including sharks, sea turtles, and marine birds, have been harmed. These animals can occasionally become trapped in plastic trash, which can seriously harm them, block their movements, damage their ability to eat properly, and restrict their ability to breathe (Omar et al., 2021).

Research and development of renewable and biodegradable polymer composites have attracted more attention in recent years due to the severe environmental harm caused by petroleum-based polymers (Li et al., 2018). Considering its adaptability and great potential for usage in a wide range of industrial applications, Polylactic Acid (PLA) is the most likely biodegradable polymer that is being developed among all bioplastics (Kamarudin et al., 2020). Due to its mechanical similarities to PET, PLA is considered as one of the most inventive replacements for existing petroleum-based polymers. Furthermore, PLA has great potential because of its great qualities, including easy processing, excellent degradability, and good mechanical qualities (particularly in strength and modulus). Despite of having greats benefits, PLA's high brittleness, low toughness, and low tensile elongation are its biggest weaknesses (Giita Silverajah et al., 2012).

Many researchers have conducted a study to enhance the mechanical characteristics of PLA by adding plasticizers (Al-Mulla et al., 2010). Plasticizers are one of the most significant additives in the production of polymer materials. Plasticizers' main purpose is to increase the flexibility and processability of polymers (Awale et al., 2018). A plasticizer enhances the plasticity of a polymer by weakening the intermolecular bond force, reducing crystallinity and increasing relative movement between molecular segments (Jia et al., 2018). The most common plasticizers are made from petroleum-based phthalate compounds. In contrast, considering their potential toxicity to humans, the use of these chemicals has generated concern (Cai et al., 2020).

Research has turned more to natural and biodegradable plasticizers made from epoxidized vegetable oil to replace petroleum-based plasticizers (Hosney et al., 2018). Due to its particularly low toxicity and wide availability, epoxidized vegetable oil as derived substance has significantly possessed great benefits, which has caused its price to rise in recent years (Jia et al., 2018). Several types of epoxidized vegetable oils have been used as the feedstock for the plasticizer such as Epoxidized Soybean Oil (ESO) (Chieng et al., 2014), Epoxidized Rubber Seed Oil (EeRSO) (Thuy et al., 2021), Epoxidized Karanja Oil (EKO) (Garcia-Garcia et al., 2020), and Epoxidized Palm Oil (EPO) (Ali et al., 2016).

However, one of the main disadvantages of using bio-plasticizers made from edible oils is that it drains resources from the food and feed chain, which might have a negative effect on the price of edible oils on the global market. Human consumption accounts for over 80% of the global production of vegetable oils which is considered as highly valuable due to its benefits to humankind. Moreover, the advantageous usage of waste coal (WCO) also tackles the issue of improper disposal of waste materials, which pose a significant risk to the environment and waste treatment facilities. The purposed of this study will investigate using Waste Cooking Oil (WCO) as the feedstock for plasticizers. Despite the limited of studies, a similar results has been reached on the use of used cooking oil as a feedstock for plasticizers (Cai et al., 2020). This study aims to fills in the gaps in modifying the PLA's properties. In terms of its mechanical properties, such as flexural strength and impact energy. This report aims to investigate the influence of adding epoxidized waste cooking oil (EWCO) to PLA. Different amounts of bio-based plasticizers will be used in this PLA blend which are Pure PLA, PLA with 2.5 %, 5 %, 7.5 % and 10 % of waste cooking oil-based plasticizer (WCOP).

2. Experimental

2.1 Materials

A 3001D poly (lactic acid) in the form of pellets was acquired from NatureWorksTM LLC. Prior being employed in the blend preparation, the polymer was dried for up to two hours at 50 °C (Giita Silverajah et al., 2012). Waste Cooking Oil (WCO) was collected from fried banana stores in Melaka. 88 % of Formic Acid, HCOOH and 30 % of Hydrogen Peroxide, H_2O_2 were obtained from Systerm Chermicals Company in Malaysia for the epoxidation process.

2.2 Epoxidized waste cooking oil (EWCO)

Production of Epoxidized Waste Cooking Oil (EWCO) was started with a 40 g of WCO and 3.7 g of HCOOH in a three-necked round bottom flask which then stirred for 30 min at 30 °C. The process was continued by adding dropwise 32 g of H_2O_2 into the flask within 30 min and followed by stirring the solution for about 7 h using a magnetic stirrer (Cai et al., 2020). Epoxidized Waste Cooking (EWCO) oil was obtained by washing the mixture with distilled water (Liu et al., 2020) as shown in Figure 1.

Figure 1: Epoxidized Waste Cooking Oil (EWCO)

2.3 Sample preparation

Pure PLA was dried for four hours at 80 °C, while the Epoxidized Waste Cooking Oil (EWCO) was kept at ambient temperature (Thuy, Duc and Liem, 2018). Prior to starting the blending process, preheating the PLA was done to prevent hydrolysis (Garcia-Garcia et al., 2020). Both PLA and EWCO were mixed manually according to the percentages shown in Table 1. After mixing, the mixtures were put into a twin-screw extruder at a temperature of between 165 °C to 180 °C. The extruded samples were then collected and crushed to produce in pellet form. Finally, the PLA blends were placed in a rectangular mold which then were heated at 220 °C for 30 s using hot press machine as shown in Figure 2.

Table 1: PLA blends with different amounts of EWCO

PLA Blends	Plasticizer amount (%)
Pure PLA	-
PLA- 2.5 % EWCO	2.5
PLA- 5 % EWCO	5
PLA- 7.5 % EWCO	7.5
PLA- 10 % EWCO	10

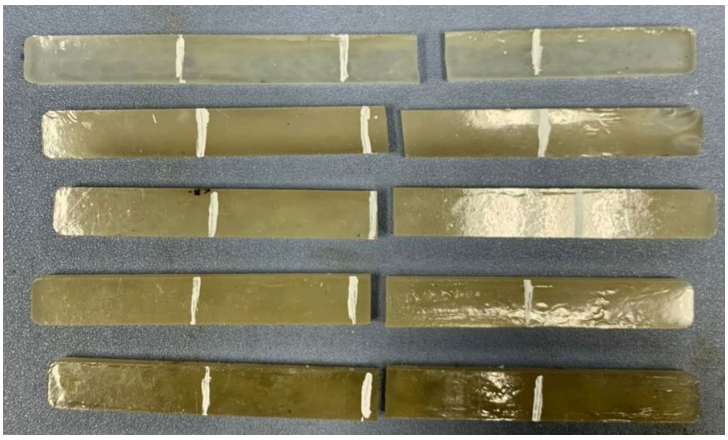

Figure 2: Sample of PLA blends

2.4 Flexural test

The flexural test was performed according to ASTM D790 as illustrated in Figure 3. A total of five rectangular samples with a dimension of 128 mm x 10 mm x 4.5 mm were produced for further test. The analysis was conducted using Floor Mounted Material Testing Machine (Instron Model 5585) at a speed of 0.2 mm/s (Jaya et al., 2018). Five sets for every sample's average result were provided.

Figure 3: Flexural testing

2.5 Impact test

Impact tests were carried out by using Universal Pendulum Impact as shown in Figure 4 below Test with referencing to ASTM D256. 5 samples with the dimensions 80 mm x 10 mm x 4.5 mm were prepared. The final result of impact strength was determined on the average of five values (Giita Silverajah et al., 2012).

3. Results and discussion

The experimental results of flexural strength properties for PLA blends are illustrated in Figure 4. Five different ratios were demonstrated which are 0 %, 2.5 %, 5 %, 7.5 % and 10 % of waste cooking oil-based plasticizer. Flexural strength is the maximum amount of flexural stress that a material can consistently hold (Ali et al., 2016). The effects of EWCO on the bending stress in the PLA blends were slightly increased from Pure PLA to PLA 2.5 % content of EWCO. However, as the content of EWCO increases to PLA 5 %, the profile tends to gradually decrease. There is a slight increment of flexural strength properties of PLA 7.5 % before decreasing to PLA 10 %. The findings demonstrate that EWCO has a plasticizing impact on the PLA matrix which also agreed in the result of Li et al. (2018), and the plasticized PLA blend displayed its optimal properties at a plasticizer content of 2.5 %.

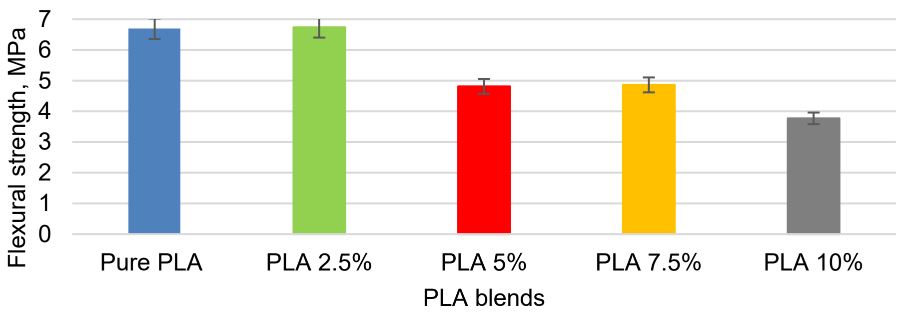

Figure 4: Flexural strength for PLA blends

Flexural extension for all PLA blends were shown in Figure 5. The trend illustrates that the flexural extension drastically increases from Pure PLA to PLA 2.5 %. It is observed that the highest flexural extension was at PLA 2.5 % content of EWCO at 0.754 mm before significantly reducing to PLA 10 % of EWCO. In contrast, PLA 10 % of EWCO has the lowest flexural extension which caused the polymer becoming more brittle. It is supported also by the results by Chieng et al., (2014). In this case, it has been shown that 2.5 % of EWCO is a sufficient amount of bio-based plasticizer that can improve PLA flexibility.

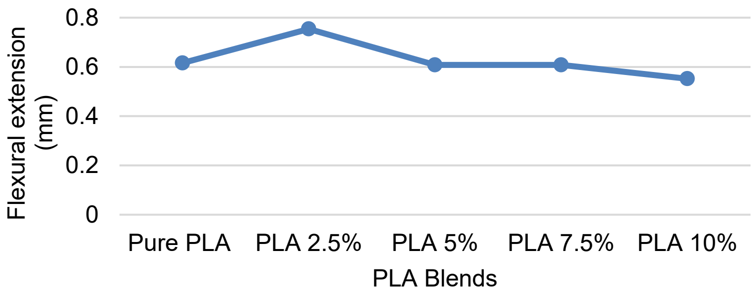

Figure 5: Flexural extension for PLA blends

Figure 6 displays the impact energy of Pure PLA and other PLA blends. It has been observed that the impact energy of PLA considerably increased with EWCO plasticizer addition until an optimal point was reached which is at PLA 2.5 % content of EWCO. The addition of EWCO after this amount will cause the trend of impact energy to decrease. According to this finding, 2.5 % of EWCO was enough to improve interactions between the PLA matrix and EWCO. Consequently, the bio- blend's durability might be increased (Thuy et al., 2021). A plasticizer is typically added to a polymer matrix to reduce brittleness brought on by strong intermolecular interactions. EWCO plasticizer thus decreases these intermolecular interactions, increasing the extensibility and flexibility of the PLA composition (Thuy et al., 2018).

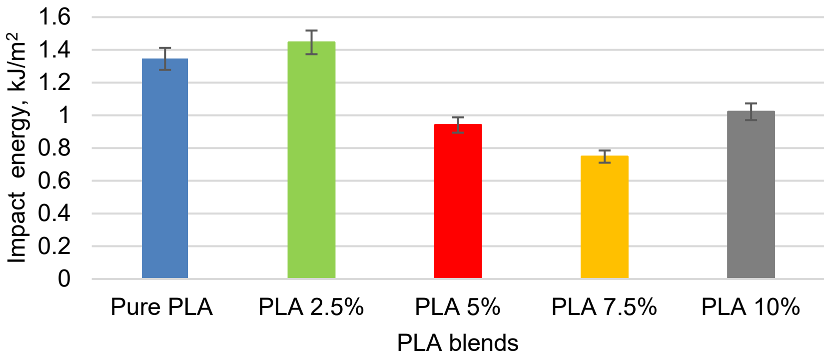

Figure 6: Impact strength for PLA blends

4. Conclusion

The flexural strength, flexural extension and impact energy of PLA and plasticized PLA were investigated in this study. Results from these analyses show that adding EWCO to PLA mixes causes the extension to increase noticeably, indicating that the samples' flexibility was increased. The increment of the flexural strength, flexural extension and impact energy reaching the optimum amount improved the flexibility and tenacity of the plasticized PLA at 6.74 MPa, 0.754 mm and 1.446 kJ/m^2. A 2.5 % waste cooking oil-based plasticizer content is the ideal amount for a PLA combination. The investigation demonstrates that EWCO might be employed in PLA as an additional plasticizer. EWCO is ideal, especially in terms of its beneficial outcomes. It functions effectively as a plasticizer and stabiliser. This study also offers significant evidence for switching to renewable, biodegradable plasticizers derived from waste cooking oil in place of petroleum-based plasticizers. WCO as a feedstock for bio-based plasticizers has many advantages, particularly for the environment.

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