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Properties of Key Lime Essential Oil Blend into Polylactide Acid/Polyethylene Glycol Film Composite

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ABSTRACT

Lime essential oil (LEO) has the potential to be incorporated into a film. Biodegradable polylactic acid (PLA) has shown potential in packaging applications. In this study, Lime extraction was carried out using a simple distillation method, and solvent casting methods were used to form the films. FT-IR result shows that the PLA primary functional group was visible at the frequency region of 495-560 cm^{-1} and 1740-1750 cm^{-1}. With the addition of polyethylene glycol (PEG) and lime essential oil, the composite shows improvement in thermal stability. Even after being heated to 500 °C, none of the three samples completely disintegrated after being given lime essential oil as an additive.

1. Introduction

Lemon, orange, and lime citrus peel are used in industrial production such as pharmaceutical, food and beverage as stated by Andersen *et al*., [1]. As a significant processed crop, citrus generates substantial wastes and products that are rich in various bioactive substances, including pectin, water-soluble and insoluble antioxidants, and essential oils as mentioned by Barkoula *et al*., [2]. If citrus peels are thrown away, they may contribute to environmental problems, most notably water pollution. This is because citrus peels contain biomaterials such as oil, pectin, and sugar, which encourage aerobic bacteria to break down biodegradable organic matter into water contaminants such as carbon dioxide, nitrates, sulphates, and phosphates. Citrus peels are a potential contributor to environmental problems because of the potential for water pollution, this issues has been pointed out by Davoodi *et al*., [3].

Essential oils and volatile oils from a variety of medicinal plants have been utilized to treat cancer, lung conditions, neurological diseases, and cardiac ailments as health-promoting agents [4]. In

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addition, essential oils and the goods that are derived from them can be found in a wide variety of industries, including but not limited to soaps, cosmetics, aromatherapy, fragrances, phytomedicine, cleansers, seasonings, meals, agriculture, and drinks [5]. Similarly, like most essential oils, it is obtained as a byproduct of the juice extraction process using centrifugation, and the resulting oil is cold pressed [6].

The effects of climate change and the depletion of our planet's natural resources are already profoundly impacting our daily lives. To protect the environment, scientists are producing biodegradable and ecologically friendly items [7]. Polylactic acid (PLA) has become the most extensively used disposable biopolymer in the world because it is biodegradable, has a high level of biocompatibility, and is transparent. The features of high strength and outstanding processability make PLA one of the most promising biopolymers. PLA is one of the most promising biodegradable polymers. As a result, PLA is one of the polymers with the highest level of biodegradability. However, because of its molecular structure and crystallization, PLA has several obvious drawbacks, some of which are a high level of brittleness, a low level of melt strength, and a small processing window. These characteristics combine to significantly restrict its application in a variety of industries [8].

Therefore, many PLA modification studies have been conducted to improve its performance [9]. In this study, PLA was reinforced with Polyethylene Glycol (PEG) to overcome the limitation of PLA. The key lime essential oil (LEO) was blend into PLA/PEG film to determine the properties of the new material of composites.

2. Methodology

2.1 Materials

The Key lime that been used in this research was purchased at local super market. The key lime used was selected in order to make sure the quality of the obtained key lime essential. The solvent that has been used in this research was chloroform was purchased at Merck KGaA. Polylactic acid was selected as a polymer in this research was purchased at cardia-bioplastics and polyethylene glycol was purchased at Sigma-Aldrich.

Tables 1 contain a list of the material specifications used in this research.

Table 1
Material details used in this study

Material	Brand
Key lime	-
Chloroform	Merck KGaA
Polylactic acid	Cardia-bioplastics
Polyethylene glycol	Sigma-Aldrich

2.2 Extraction of Key Lime Essential Oil (LEO)

The oil was extracted from the key lime peels through a simple distillation process. First, the citrus fruit was peeled and chopped into small pieces. For the extraction, 100 g were measured. The peels were then added to the round-bottomed boiling flask. In the flask, 250 mL of water was used as the solvent. The temperature was set to 100 degrees Celsius. As the liquid is heated, vapours with a low boiling point are produced. The duration of this procedure was three hours. The oil mixture was then separated using a separating funnel.

2.3 Gas Chromatography Method

Component PLA/PEG/LEO were determined using gas chromatography. Gas chromatography was setting accordance to Table 2 below.

Table 2
Gas chromatography setting

Column type	Phenomenex ZB-wax plus; 30m x 0.25mm; 0.25µm
Carrier gas	Helium
Flow	1.0 ml/min
Oven	45 °C,6 min,3 °C /min, 90 °C, 5 °C /min, 180 °C, 16 min
Detector	220
Injector	220
Injection volume	1µL
Split	1:100
Run time	55 min

2.4 Incorporation of Key Lime Essential Oil into PLA/PEG/LEO Film

A solvent casting process was used to prepare a polylactic acid/polyethylene glycol/lime essential oil film (PLA/PEG/LEO). PLA (1 g) and PEG (0.1 g) were weighted, vigorously dry mixed, and then added to a glass beaker with 20 mg chloroform and stirred until the polymer dissolved. The essential oils (5, 15, and 40% w/w of PLA/PEG) were put into the PLA/PEG solutions and blended for an additional 15 minutes to ensure that the lime essential oils were wholly incorporated into the film solutions. The resulting mixture was placed onto a (10 cm×1.5 cm) glass petri dish. The chloroform was evaporated in a fume hood at room temperature. Peeled dried films were removed from the glass plates and stored at room temperature (25°C) in a desiccator until further usage.

2.5 Thermal Properties
2.5.1 Differential scanning Calorimetry (DSC)

The glass transition and crystallisation were determined using differential scanning calorimetry. Melting temperatures of PLA/PEG/LEO samples (Perkin-Elmer Diamond DSC). 5 mg samples were heated at a rate of 5 °C step/min between 30 and 200°C under a constant flow rate of 20 mL/min nitrogen gas purging through the calorimeter. After 1 minute at 200°C, the sample was cooled to 30°C and then heated to 200°C at the same rate of 5°C /min.

2.5.2 Thermogravimetric analysis (TGA)

The thermal stability of PLA/PEG/LEO samples was studied using a Perkin-Elmer TGA machine and 5-10 mg of samples heated at a rate of 10 °C per minute from room temperature to 500 °C. Each sample's initial and final degradation temperatures, as well as the accompanying percentage weight loss, were recorded.

2.5.3 Fourier transform infrared spectroscopy (FT-IR)

Fourier transform infrared spectroscopy of PLA/PEG/LEO film determined their functional group and carbon structure using Fourier transform infrared spectroscopy (FT-IR). Spectra were collected

for all the samples by recording 32 scans in % transmission mode in the range of 4000 cm^{-1} – 400 cm^{-1}. Peak deconvolutions were performed using Perkin Elmer GRAMS software.

3. Results

3.1 Characterization of Key Lime Essential Oil

Figure 1 shows a chromatogram of the key lime essential oil standard. The graph shows that the beta-pinene peak occurred at minute 5.08, the limonene peak occurred at minute 8.71, and the gamma-terpinen peak occurred at minute 10.78. These VOCs were any one of the hundreds of aromatic chemicals that make up essential oils.

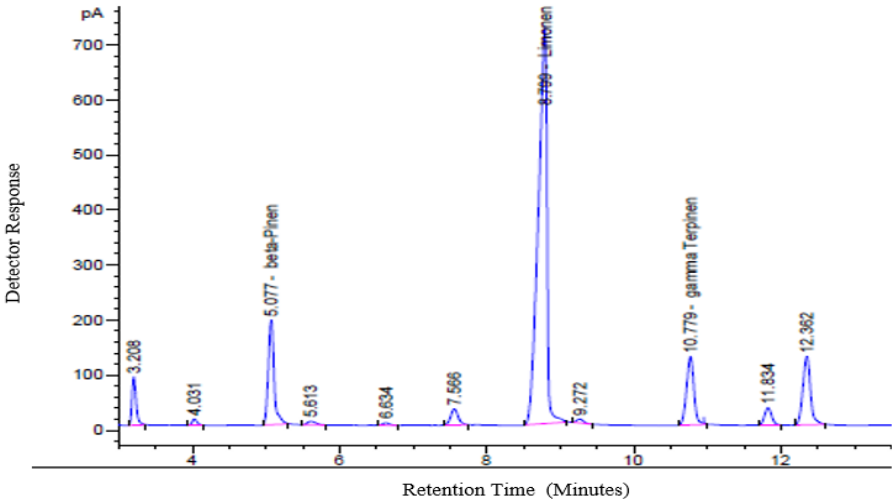

Fig. 1. Gas chromatography of key lime essential oil standard

Figure 2 shows a chromatogram for obtained key lime essential; The graph shows that the peak of beta-pinene concentration occurred at minute 4.88, the peak of limonene concentration occurred at minute 8.92, and the peak of gamma-terpinene concentration occurred at minute 10.78. The findings indicate that the extraction of essential oil was successful because the peaks in Figures 1 and 2 are comparable to one another. Figure 1 and Figure 2 also show that limonene has the higher concentration compare to the gamma Terpene and beta pinen, this has been proved in previous study [10,11].

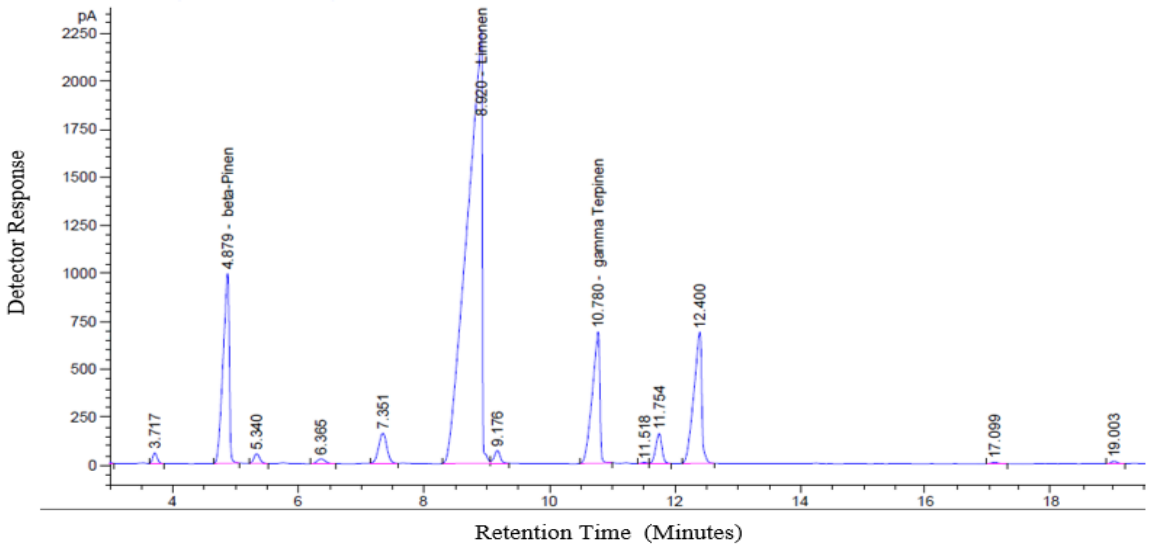

Fig. 2. Gas chromatography of key lime essential oil

3.2 Fourier Transform Infrared Spectroscopy (FT-IR)

The C-H stretch's distinctive bands, which are between 2877 and 2797 cm^{-1}, are shown in Figure 3. In Figure 3, the carboxylic acid O-H stretch is highly diagnosed at 3318 cm^{-1}, and in Figure 3, it is highly diagnosed at 3250 cm^{-1}. The characteristic absorption for the C=C stretch occurs at 1637 cm^{-1} (Figure 3) and 1640-1585 cm^{-1} (see Figure 3). The characteristic bands depicted in Figure 3 correspond to the C=O stretch at 1763 cm^{-1}.

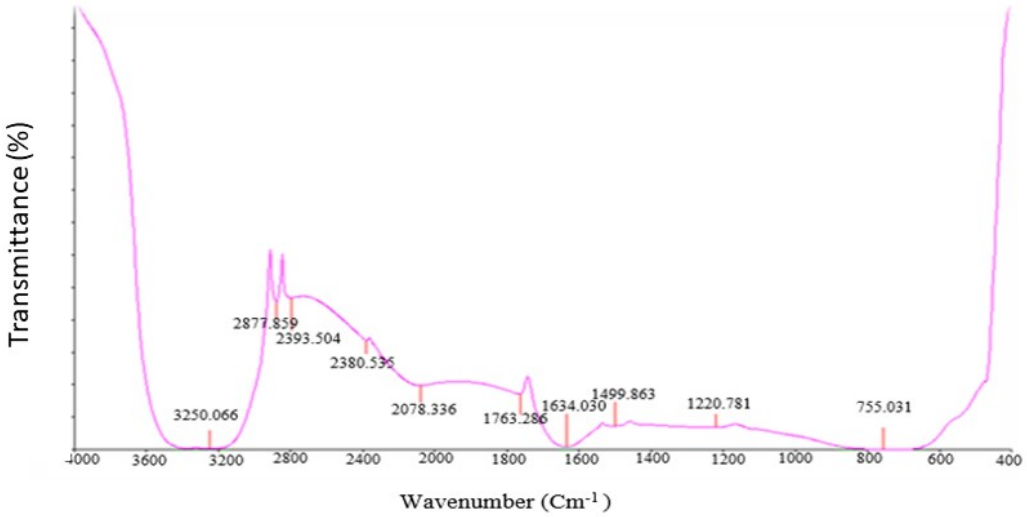

Fig. 3. FT-IR spectra of key lime essential oil

FT-IR spectroscopy is one of the most sophisticated methods for assessing changes in the conformations of films. The PLA composite's FT-IR spectra are displayed in Figure 4. FT-IR spectroscopy is one of the most advanced tools for determining changes in the conformations of films. According to the report, the primary functional group of PLA appeared in the C=O group-assigned frequency ranges of 495-560 cm^{-1} and 1740-1750 cm^{-1} aligned with previous study[12,13]. From the previous study, when PEG was added to the PLA composite, there was no noticeable change

at the peaks [14]. Therefore, the similar natural structure of PLA and PEG consists of carbon and oxygen atoms. This research confirmed that the carbonyl group's absorption shift peak of PLA and PEG films moved from 502 cm^{-1} to 587 cm^{-1}. It demonstrated that PEG has good PLA miscibility, and low molecular weight PEG enhanced PLA miscibility in line with prior studies [12]. There was a change in the intensity of the peak at 726 cm^{-1} after the additional of lime essential oil into the composite film. This was caused by the C=O group in key lime essential oil (Figure 3) merging with the C=O group in the composite.

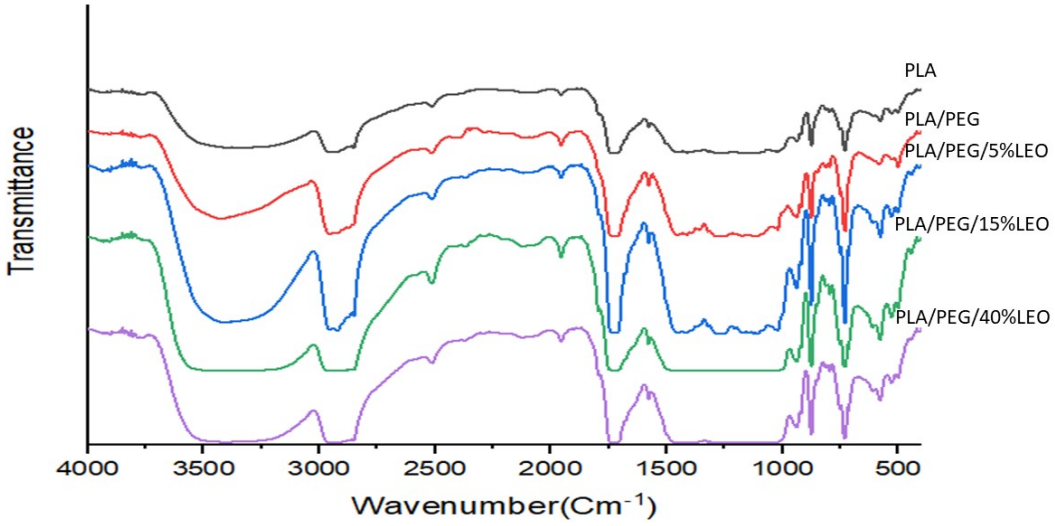

Fig. 4. FT-IR spectra of film

3.3 Differential Scanning Calorimetry (DSC)

DSC thermograms revealed the presence of two distinct thermal transitions: the glass transition, indicated by the glass transition temperature (T_g), and the crystallization process, characterized by the crystallization temperature (T_c). By heating the amorphous material, T_g is defined as a physical change from the way of flexibility to the way of glass Consistent with previous studies [15]. The values obtained are reported in Table 3. Pure PLA It was discovered that the glass transition temperature was 41 °C, which is highly comparable to what was stated in the [16] which is at 42.6 °C, and with addition of PEG increased the composite T_g by about 14°C, which makes T_g for PLA/PEG composite 55°C. The addition of LEO also increased T_g for Composite, which makes T_g for PLA/PEG/5%LEO 59°C, 61°C for PLA/PEG/15%LEO, and T_g for PLA/PEG/40%LEO is 63°C. According to this data, adding PEG and LEO slightly increases the composite's thermal stability.

Table 3
Data obtained from DSC analysis for PLA composites

Sample	Glass Transition (T_g, °C)	Crystallization Temperature (T_c, °C)
PLA	41	83
PLA/PEG	55	99
PLA/PEG/5% LEO	59	101
PLA/PEG/15% LEO	61	102
PLA/PEG/40% LEO	63	105

Figure 5 also shows that pure PLA began to crystallize at 83°C, and the temperature increased when pure PLA and PEG were added at 99°C. A similar behaviour also detected by [17]. Crystallization

also slightly increased when lime essential oil was added to the composite where make T_g for PLA/PEG/5%LEO is at 101°C, 102°C for PLA/PEG/15%LEO, and 105°C for PLA/PEG/40%LEO. The findings unequivocally show that increasing PEG and lime content in PLA composite can boost crystallization temperature.

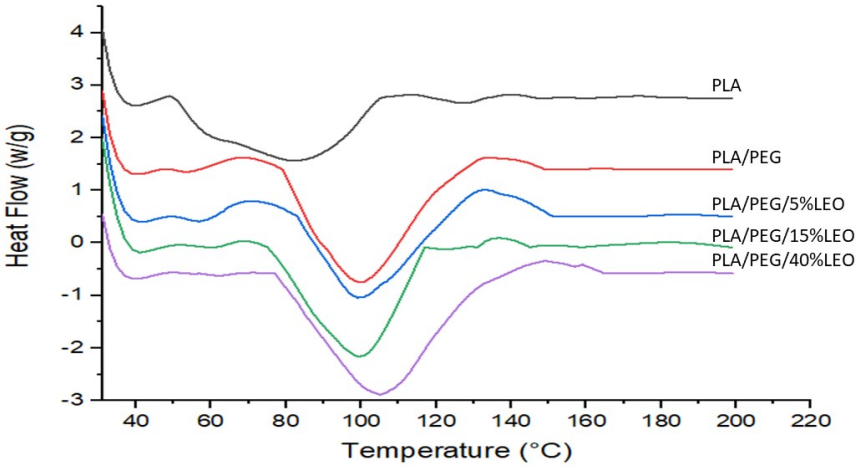

Fig. 5. DSC thermogram of film

3.4 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) measurements were carried out so that an investigation into the thermal characteristics of the composite could be carried out. As can be seen in Figure 6, the temperature at which pure PLA begins to decompose is 277°C. After reaching this temperature, the loss in weight continued, and the final degree temperature for PLA was determined to be 363°C, align by a previous study [18]. With the addition of PEG in the composite, the composite start decomposing at 256°C, much lower than pure PLA, and attains a final degree temperature at 448°C, in accordance with previous study[19,20]. PLA/PEG/5% LEO film shows that the sample start decomposes at 270°C, whereas PLA/PEG/15% LEO film starts to decompose at 275°C lastly is a composite with higher additional percentage of lime essential oil start 280°C. According to the findings, the incorporation of lime essential oil leads to an increase in the temperature of the sample's initial decomposition. With the addition of lime essential oil, none of the three samples fully decomposed even after being heated to 500°C.

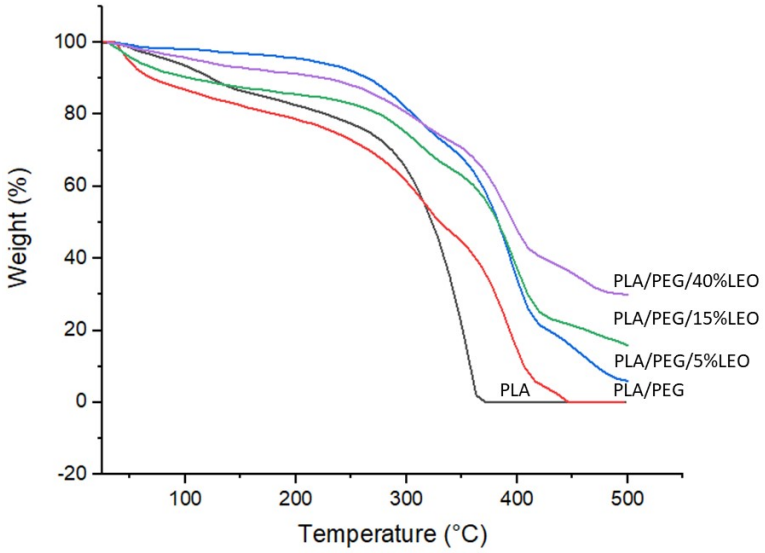

Fig. 6. Thermogravimetric of film

4. Conclusions

With a simple distillation method Key lime essential oil was successfully extracted proven by gas chromatography. PLA was incorporated into composite by casting method and undergo FT-IR to assessing changes in the conformations of films. There was no noticeable change at the peaks since PLA and PEG consists of similar natural structure. Glass transition of composite gradually increase with the addition of PEG and Key lime essential oil. The same thing occurs with crystallization temperature. For thermal stability, a composite without PEG has higher thermal stability than composite with PEG.

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