The effect of kaffir lime (Citrus hystrix DC) essential oil on bioplastic derived from cassava peel waste

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Abstract. Kaffir lime essential oil is reported contain a biologically active secondary metabolite from the class of terpenoid. It was reported active as antibacterial, antioxidant, and anticancer. Combination of this bioactive essential oil to afford bioplastic or biodegradable plastic will open their future applications in industry and medicine. This paper report the characteristic of the combining of kaffir lime essential with starch from cassava peel waste to produce bioplastic. The FTIR spectroscopy, SEM, XRD and elasticity test was reported to the bioplastic produced. In short, bioplastic prepared from both starting materials are able to be made. The appearance is clear and transparent. The FTIR spectra also provide a combination of both functional groups, and some fractures found to the bioplastic without addition of kaffir lime essential oil. Interestingly, elasticity improves for bioplastic composed of essential oil.

1. Introduction
Essential oil produces from kaffir lime (Citrus hystrix DC) by steam distillation shows many bioactivities, such as antibacterial [1, 2], antioxidant [3], and anticancer [4, 5]. This oil is composed of sesquiterpene (C15) and monoterpen (C10) class of the terpenoid secondary metabolite [6] group (Fig 2). The structure of both groups have hydroxyl- (OH), carbonyl- (C=O), and carboxyl- (O=CO-R) ester (Figure 1), that is able to be used interact to the other polar groups from the other materials. This interaction can undergo via hydrogen bonding, electronic induction and or nonpolar-nonpolar interaction, similar to that glycerin does act as plasticizer in plastic material[7, 8]. With the longer carbon chain from 10 in monoterpen to 15 in sesquiterpene structures increase their hydrophobicity. In other hand, East Java province also reported to be the producer of cassava (Manihot esculenta). The average production is about 3.2 kTon per year during the last decade, and is mostly used as raw material for cassava flour, traditional food-fermented product, and cracker-based snacks. However, this production lines provide the peel’s waste in average 10-15% from the total of dry weight. The disposed waste still contains starch in about 10% as well (Fig 1). Previously, it has been reported to modification into the acetyloxy- and oleic acid ester of the starch peel’s waste [9]. This paper is disclosed the application of starch prepared from cassava peel’s waste for bioplastic production. The addition of kaffir lime essential oil (EO) toward the bioplastic increases not only the elasticity or strength and elongation stability of bioplastic, but also the smoothness and integrity of bioplastic surface.
2. Experiment section
2.1. Material and chemicals
Sample of cassava is bought from local farmer in Malang region, East Java. The taxonomy is known as Manihot esculenta as previously reported. Meanwhile the kaffir lime (Citrus hystrix DC) essential oil (EO) is bought from Institute Atsiri of Brawijaya University, Malang. Some chemicals used for research include citric acid (CA) (Merck), and glycerol (Merck).

2.2. Instrument analysis
Spectrometer used for analysis include infrared spectra measurement using FTIR spectrophotometer (Shimadzu), scanning electron microscope (SEM) brand of Hitachi TM-3000, x-ray diffraction (XRD) PanAnalytical type E’xpert Pro, elongation and tensil strength measurement using Imada Force ZP-200N.
2.3. Bioplastic preparation
A homogeneous solution of dried of peel’s waste starch (5.0 g) is added glycerol (1.5 mL). Then, kaffir lime essential oil (EO) (0.5 mL) and citric acid (0.7 g) is added. This mixture is stirred for 45 min, and heated to 80 °C until a viscosous mixture is formed. This mixture is poured into bioplastic template, made of a glass plate (10x10 cm) and dried in oven at 50 °C for 48 h. The bioplastic resulted is further analysis for characterization. This procedure is labelled as sample 1. Others separated procedures are undertaken with different addition. Sample 2, is prepared without addition of essential oil and using citric acid 0.7 g. Sample 3 uses essential oil 0.5 mL and without addition of citric acid. Sample 4 is prepared without the addition of essential oil and citric acid.

3. Result and discussion
The bioplastic prepared from cassava peel’s waste are able to be produced with starch as the main composition, and additive plasticizing agent of glycerol (Figure 3). Four different mixtures of bioplastic are prepared with different addition of kaffir lime essential oil (EO) and citric acid. Addition of the EO on the bioplastic mixture made the surface smooth and denser. No wrinkle is observed (Figure 1a and b), however without addition EO made bioplastic feature crack and coarse (Figure 3c and d). SEM micrograph also give more detail features morphology of bioplastic in the surface (Figure 4). EO of kaffir lime is predicted to affect the smooth of bioplastic surface (Figure 4a and b). But a coarse and less dense surface with pore or hole observe is observed for bioplastic without addition of EO from kaffir lime (Figure 4c and d).

![Figure 3. Bioplastic prepared from starch of cassava peel waste with and without addition of kaffir lime essential oil (EO) and citric acid. (a) sample 1, (b) sample 2, (c) sample 3, and (d) sample 4.](image)

The physical analysis toward bioplastic is also undertaken using FTIR spectrophotometer. In some cases, blending process all of reactants such as starch, essential oil, plasticizer and citric acid can affect the integrity of bioplastic resulted. Homogeneous mixing can be represented by a complete solvation and is indicated from the combination of the FTIR spectra. The result (Figure 5), indicate FTIR spectra consists of the components of the starting materials. Hydroxyl-group is observed in between 3500-3200 cm⁻¹. It is a broad band that correlate to hydroxyl-group (O-H) of carboxylic acid (RCOOH) compounds as well. The carbonyl-group (C=O) is detected at 1726 cm⁻¹ and the double bond of carbon-carbon (C=C) alkene group is recorded presence in 1647 cm⁻¹. Meanwhile the band for
single bond of (C-O-C) ester found is between 1200-1001 cm$^{-1}$. All these bands correlate to the starch, EO, and citric acid that are mixed in bioplastic.

**Figure 4.** Photograph of scanning electron microscope.

**Figure 5.** Infra red spectra of bioplastic prepared with kaffir lime essential oil and starch derived from cassava peel waste.
Even though the FTIR spectra indicate a blend and homogeneous mixtures, x-ray diffraction spectra slightly give a detail accuracy of homogeneous mixtures (Figure 6). The bioplastic has a low crystallinity. An amorphous mixture is generally observed, but combination peaks of all reagent composed of the bioplastic clearly represented (sample 1, sample 2 and sample 4).

![Figure 6. XRD diffractogram of bioplastic.](image)

Moreover, the effect of addition of EO from kaffir lime increase the stability in tensile strength of bioplastic (Figure 7). The bioplastic made of EO resist the stretching energy until 1.8 N/cm and able to elongate 85% (Sample 1) and about 65% (Sample 2). But, a low stability is observed for bioplastic made of cassava peel’s waste starch without addition of EO from kaffir lime nor citric acid.

![Figure 7. Tensil strength and elongation measurement of bioplastic prepared from cassava peel waste with and without kaffir lime essential oil (EO).](image)
4. Conclusion
The cassava peel’s waste can derive starch that is further applied for bioplastic. Combining kaffir lime essential oil (EO) into bioplastic create improvement in tensile strength stability and that increase elongation of bioplastic by 85% longer. This result can pave the way for further intensive research by improvement and optimization for cassava starch for starting material of bioplastic production.

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