BIODEGRADABLE COATING FROM AGATHIS ALBA

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Abstract :
The adhesive property of copal makes it as a potential coating onto aluminum foil to replace polyethylene. This research aimed to develop copal-based coating. The coating was prepared by extracting the copal in ethyl acetate and dipping the aluminium foil in ethyl acetate soluble extract of copal. The characterization of coating included its thickness, weight, thermal and chemical resistance, and biodegradation. The results showed that the coating thickness and weight increased as the copal concentration and dipping frequency increased. Thermal resistance test showed that the coating melted after being heated at 110°C for 30 min. Copal-based coating was resistant to acidic solution (pH 4.0), water, and coconut oil, but was deteriorated in detergent 1% (w/v) and basic solution (pH 10.0). Biodegradability test using *Pseudomonas aeruginosa* showed weight reduction of 76.82% in 30 days.

Keywords*:* Agathis alba; copal; biodegradable packaging; dip coating.

1. Introduction

Coating on aluminium foil was developed to give additional protection against chemical and physical stress and to improve the mechanical properties (Holovach 2012). The most commercial coating onto the aluminium foil is polyethylene due to its superior mechanical and protective properties. However, the use of polyethylene as packaging material has caused massive issues in its production and disposal. Four percent of petroleum has been as raw material for plastic and the demands are still increasing while oil fossil stock is limited [Park (2006)]. Moreover, the disposal of such plastic has been a threat to both land and marine environments. The economic value of biopolymers increases to a significant extent. The annual market demand was reported about 500 000 - 10 000 000 ton [Flieger *et al.* (2003)]. Therefore, this research aimed to develop copal-based coating and to evaluate some fundamental properties and biodegradation rate.

2. Materials and Methods

2.1. *Materials*

Copal resin (*Agathis alba*) was purchased from Baturaden Botanical Garden (Central Java). Hexane, ethyl acetate, ethanol, HCl, and NaOH for extraction and characterization were reagent grade (Merck). Tryptose Soya Broth (TSB), Nutrient Agar (NA), and NaCl to evaluate the coating biodegradability were purchased from Oxoid. *Pseudomonas aeruginosa* was obtained from Laboratory of Microbiology and Fermentation, Atma Jaya Catholic University. Other materials such as aluminium foil with thickness of 0.02 mm, filter paper, coconut oil, and detergent were bought from local market. Specific equipments used in this research were micrometer (Mitutoyo), oven (Memmert), py-GC/MS (QP 2010 Shimadzu), vacuum rotary evaporator (Buchi R-215), and spectrophotometer VIS (Thermospectronic).

2.2. *Methods*

This study was divided into several steps, i.e. copal extraction and coating preparation, characterization the thermal and chemical resistance of coating, and evaluation coating biodegradability.

2.2.1. Copal extraction and coating preparation

Three series of copal extracts were prepared by suspended the copal in hexane, ethyl acetate, and ethanol, each was made at 10, 20, and 30% (w/v). The suspension was stirred at medium speed for 24 h subsequently followed by filtration to remove insoluble materials. A small volume of filtrate was separated and the chemical compounds in the extract were determined using py-GC/MS after the solvent was evaporated using vacuum rotary evaporator.

The filtrate was used to dip aluminium foil for 25 s before being withdrawn and evaporated at room temperature. The dipping was conducted once, two, three, and four times with evaporation time of 45 min between two consecutive dipping. The thickness and weight of coating were measured using Mitutoyo and analytical balance, respectively. Coating with uniform thickness was selected for further analysis.

2.2.2. Characterization thermal and chemical resistance of coating

The thermal resistance of coating was tested by incubation the coating in oven at 90-120°C for 30 min and any changes, both visual and weight were observed. Uncoated aluminium foil was also tested as negative control and polyethylene-coated aluminium foil was used as positive control.

To evaluate coating resistance towards some solvents, coating was immersed in hydrophilic and hydrophobic solvents and in surfactant for 24 hours at room temperature. The hydrophilic solvent was distilled water while the hydrophobic one was coconut oil. Commercial detergent solution (1% w/v) was used as the representative of surfactant. Both visual and weight changes were noticed. Uncoated aluminium foil was also tested as negative control and polyethylene-coated aluminium foil was used as positive control.

To evaluate coating resistance towards acid and base, the coating was immersed in HCl pH 4.0 and NaOH pH 10.0 for 24 hours at room temperature. The weight changes were measured and physical changes were observed visually. Uncoated aluminium foil was also tested as negative control and polyethylene-coated aluminium foil was used as positive control. All tests were done triplicate.

2.2.3. Biodegradability evaluation

P. aeruginosa was inoculated in 15 ml TSB until the optical density at 600 nm reached 0.132 (0.5 McFarland) [Dutta *et al*. (2010)]. Subsequently, copal-based coating was immersed in TSB and incubated in shaking incubator at room temperature. On the 12^{th} day, 15 ml TSB was added to sample to give nutrition for the bacteria. On day 10, 20, and 30 of incubation, the coated-aluminium foil was withdrawn from media, rinsed, dried, and weighed. This test was done in triplo. Polyethylene-coated aluminium foil was used as control. Biodegradation was calculated using Eq. (1).

$$\mathrm{b} = \frac{W_t - W_o}{W_o} x100\% \qquad (1)$$

3. Results and Discussion

3.1. *Copal extraction*

Copal was soluble in organic solvents. However, due to its impurities such as ash, sand, and cellulose, copal extraction yielded some insoluble materials. The insoluble matter of copal ranged from 4.92% (w/w) to 16.74% (w/w). This data was in accordance with Waluyo *et al.* (2004) that reported the impurities of copal were 9.7-23.3% (w/w).

The chemical compounds of ethyl acetate soluble extract of copal could not be identified well. There were only four compounds which could be predicted with the similarity index 90% or more (Table 1). The composition of *A. alba* was different from that of copal from Sukabumi or Ternate. That copal has scientific name *A. loranthifolia.* The former contained limonene, ethylene oxide hexamer, *cis*-limonene oxide, toluene, *trans*-carveol, 2-siclohexane-1-one, *trans*-limonene oxide, and alpha pinene, and the later contained limonene, ethylene oxide hexamer, preludin, toluene, carveol 1, 2-siclohexane-1-one, acetat acid, hexaethylen glycol, champhen, and *trans*-limonene oxide [Resmeiliana (2011)].

Table 1. Chemical compounds of ethyl acetate soluble extract of copal with similarity index ≥90%

Name	Formula	%
2,3-Dimethylnaphthalene	$C_{12}H_{12}$	5.77
2-Cyclopentene-1-carboxylic acid, 1,2,3-trimethyl-	$C_9H_{14}O_2$	2.39
Limonene oxide	$C_{10}H_{16}O$	0.88
2-Butenone	C_4H_6O	0.81

Different extracting solvent resulted in different components in the extracts; ethyl acetate produced the clearest yellow soluble extract among all tested solvents. This result indicated that there were different copal constituents for each solvent used. When each filtrate was used to develop coating by dipping, hexane soluble fraction resulted in brittle coating so that it almost had no functional properties to protect aluminium foil. On the other hand, it is difficult to remove the ethanol insoluble matter by filtration. Therefore, ethyl acetate seemed the best solvent to develop copal-based coating on aluminium.

3.2. *Coating characteristics*

Ethyl acetate soluble fraction of copal was potential to be used as coating onto aluminium foil. It produced clear and glossy film and it attached strongly onto the aluminium foil. Both dipping frequency and copal concentration determined the thickness and weight of coating (Fig. 1). The more the dipping frequency, the thicker and the heavier the coating was. The same effect was also given by the copal concentration.

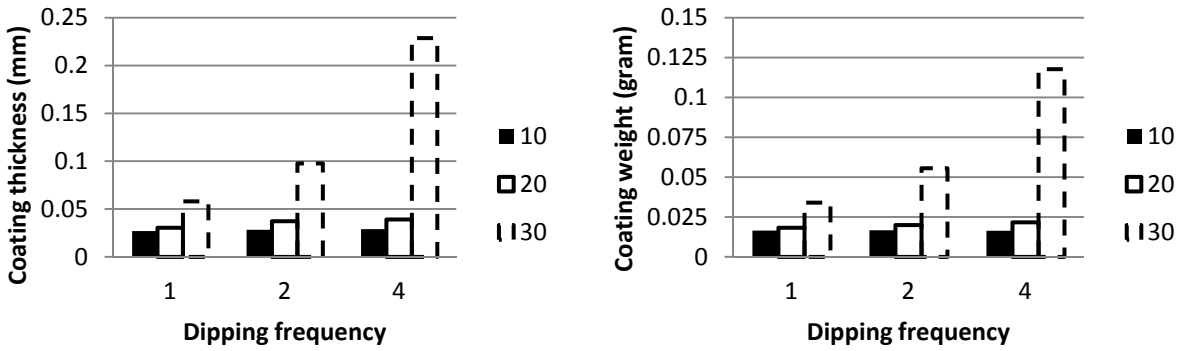

Fig. 1. Coating thickness and weight in some dipping frequency.

The thermal resistance test showed that the copal-based coating remained good after being heated at 90 and 100 ^{o}C for 30 min. However, it became yellow and sticky after being heated at 110°C for 30 minutes. It indicated that this coating could not be applied in such products which involving that condition. This thermal characteristic was similar to low density polyethylene (LDPE) but inferior to linear low density polyethylene (LLDPE) and high density polyethylene (HDPE), which had melting point about 122°C and 135°C, respectively [Habib *et al.* (2011)]. Compared to other biocoating, such as stone dammar-based coating, copal-based coating was more heat resistant. Stone dammar-based coating melted at 70-80°C [Wulandari (2011)].

Chemical resistance test showed that copal-based coating was inert in water and coconut oil, similar to uncoated aluminium foil. However, it was completely detached after being immersed in detergent 1% (w/v), but it was inert in acidic solution (pH 4.0). In basic solution (pH 10.0), the coating became white and swollen but it was still attached on aluminium foil. Uncoated aluminium foil had corroded in pH 4.0 and pH 10.0 because of the amphoteric properties of aluminium. Therefore, copal-based coating showed its functionality to protect aluminium in acidic condition, but the coating was not stable in detergent and basic solution.

The deterioration of copal-based coating in 1% (w/v) detergent was probably caused by the activity of surfactant which lowered the surface tension between coating and water [Koolman and Roehm (2005)]. The hydrophobic site of surfactant interacted with the coating so that the coating was detached. However, the detached coating was not soluble in water. Due to its hydrophobicity, it was insoluble in water. In all of chemical resistance tests, polyethylene-based coating was inert.

The biodegradability test showed that the coating was biodegradable. Using *P. aeruginosa* as biodegrading agent under aerobic condition, the biodegradation rate of copal-based coating was about 3%/day (Fig. 2). Neither weight reduction nor biofilm formation occurred in polyethylene-based coating. It should be noted that the first lag phase of biodegradation was missed, but it was clearly seen second period of biodegradation. The addition TSB, which each liter of broth is composed of tryptone (17.0 g), soytone (3.0 g), glucose (2.5 g), sodium chloride (5.0 g), and dipotassium hydrogen phosphate (2.5 g) [BD (2008)], supplied the nutrition for bacteria, so that the population increased and resulting in better biodegradation activity. It also indicated that the coating was not toxic to *P. aeruginosa*. The uncoated aluminium has not being biodegraded by *P. aeruginosa* yet after 30 days of incubation, even though the bacteria formed yellow and detachable biofilm.

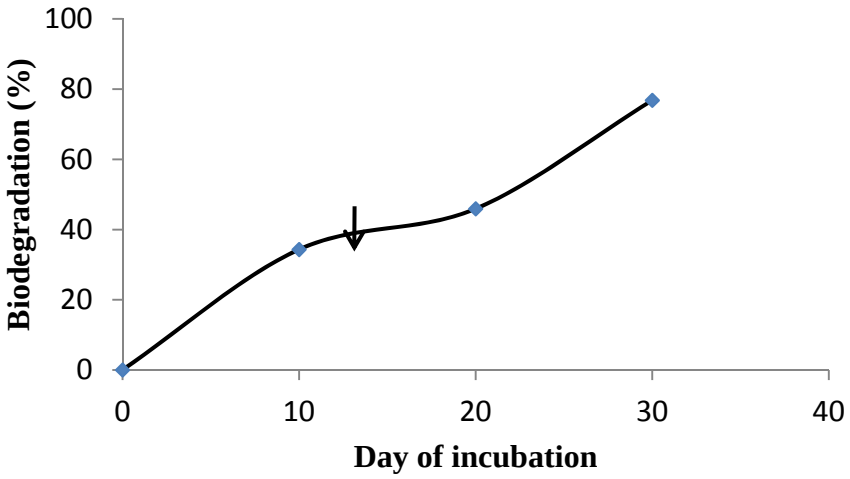

Fig. 2. Copal coating biodegradation by *P. aeruginosa*.

The biodegradation rate of copal-based coating was slower than that of polycaprolactone (PCL). Salgado *et al.* (2012) described the biodegradation of PCL at 50 °C by a thermotolerant *Aspergillus* sp was 6 d and degradation products were identified as succinic, butyric, valeric and caproic acids. Flieger *et al.* (2003) thought that it was too fast because PCL bags degraded before reaching the customers. The rate of biodegradation depended on the microbial community and the biopolymer composition as well. Flieger *et al.* (2003) reported that polyvinylalcohol (PVA) usually biodegrades in microbial active environments within 5–6 weeks but Huang *et al.* (2002) found that the fungus *Phanerochaete chrysosporium* degraded 73 % of PVA in water within 5 d.

Generally, the biodegradation of resin started by the adhesion of microorganism through hydrophobic-hydrophilic interaction to substrate before the biofilm appeared [Terada *et al*. (2006)]. The microorganisms secreted enzymes to utilize resin as the carbon source. The enzymatic processes involved oxidation and hydroxylation before the substrate was used as carbon source in citric acid cycle and CO_2 was produced (Doménech-Carbó *et al*. 2006).

P. aeruginosa was reported to be capable of producing alkane-monooxygenase as oxidation agent and alkane-hydroxylases which added hydroxyl groups to substrate [Smits *et al*. (2002)] [Kloos *et al*. (2006)]. Broth culture technique is more favorable than soil burial test to get fast result due to direct exposure of the films to the microbes. It took 30 days for copal coating to degrade almost completely using *P. aeruginosa*. In comparison, Shimpi *et al*. (2012) reported that *P. aeruginosa* degraded only 10% w/w of Poly(lactic acid) (PLA)-epoxide blend in 28 days.

4. Conclusion

Copal resin from *A. alba* is potential to be used as biocoating onto aluminium foil. It adheres strongly on the aluminium foil, has a glossy appearance, and has no odor. In addition, it has some important strong points, i.e. hydrophobic, biodegradable, and not toxic to the tested microorganism. Its thermal resistance is comparable to LDPE but inferior to HDPE or LLDPE films. However, the chemical resistance of copal-based coating, especially against base and detergent need to be improved before it can be used for commercial coating. Some strategies such as applying additive or mixing with other biopolymer should be investigated to improve thermal and chemical resistance without altering its superior properties.

Acknowledgments

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