Characterization of active paper packaging incorporated with ginger pulp oleoresin

T Wiastuti, L U Khasanah*, Kawiji, W Atmaka, G J Manuhara, R Utami
Food Science and Technology, Sebelas Maret University, Jl. Ir. Sutami 36A Kentingan, Surakarta, Indonesia

*Email: liaumikhasanah@yahoo.co.id

Abstract. Utilization of ginger pulp waste from herbal medicine and instant drinks industry in Indonesia currently used for fertilizer and fuel, whereas the ginger pulp still contains high oleoresin. Active paper packaging were developed incorporated with ginger pulp oleoresin (0%, 2%, 4%, and 6% w/w). Physical (thickness, tensile strength, and folding endurance, moisture content), sensory characteristics and antimicrobial activity of the active paper were evaluated. Selected active paper then were chemically characterized (functional groups). The additional of ginger pulp oleoresin levels are reduced tensile strength, folding endurance and sensory characteristic (color, texture and overall) and increased antimicrobial activity. Due to physical, sensory characteristic and antimicrobial activity, active paper with 2% ginger pulp oleoresin incorporation was selected. Characteristics of selected paper were 9.93% of water content; 0.81 mm of thickness; 0.54 N / mm of tensile strength; 0.30 of folding endurance; 8.43 mm inhibits the growth of _Pseudomonas fluorescence_ and 27.86 mm inhibits the growth of _Aspergillus niger_ (antimicrobial activity) and neutral preference response for sensory properties. For chemical characteristic, selected paper had OH functional group of ginger in 3422.83 cm⁻¹ of wave number and indicated contain red ginger active compounds.

1. Introduction
Ginger pulp waste was produced from herbal medicine and instant drinks industry or distillation stage. In Indonesia, ginger pulp waste currently used for fertilizer and fuel, whereas the ginger pulp still contains high oleoresin. Ginger pulp waste from UD Yogyakarta contains high oleoresin. Ginger pulp oleoresin contains Zingiber (37.13%). Zingiberene of ginger oleoresin decreased because of encapsulation (1.5%) [1]. An active compound from ginger pulp oleoresin also was affected by the extraction process. Extraction above 45°C, Gingerol decomposed into Shogaol that less quality than Gingerol [2].

Packaging technology widely developed. One of the innovative packaging technology development is active packaging. Active packaging can protect product quality and shelf life [3]. Active packaging was developed to modify active the internal environment. It has the active interaction with materials package and foodstuffs that could extend the shelf life. The systems of active packaging were O₂/CO₂ scavengers, CO₂/ethanol emitting systems, ethylene and moisture absorption systems, and antimicrobial/antioxidant releasing/containing systems [4]. Antimicrobial packaging made by incorporation and immobilization of antimicrobial agents or surface coating [5].
The paper packaging has bad barrier properties that unsuitable for prolong storage. To increase barrier properties of paper, the paper made by coating, laminating or adding by wax or resin [6]. The paper could be formed as active packaging because of the pore structure. Antimicrobial agent absorbed in pores that could increase the paper materials activity such as vapor and gas permeability, physical power, optical properties, surface properties and antimicrobial activity. The antimicrobial agent of packaging materials can diffuse in a food product (migration process) and extended product shelf life [7]. The active paper developed in several countries such as Japan, Italy, India and other [3].

The ginger has antimicrobial activity. Ginger oleoresin from Vietnam has high antimicrobial activity on Gram (+) bacteria and Gram (-) bacteria [8]. 0.5% of ginger essential oil incorporated into uwi starch edible film could inhibit Escherichia coli growth. Antibacterial compounds of ginger essential oil were gingerol, geraniol, zingiberene, zingerone, paradol and shogaol [9]. Antifungal activity of ginger oil was recorded 7.7-13.02 mm of zone inhibition for tested fungal strains. The antifungal compound of ginger was gingerol, gingerdiol and shagelol. [10, 11, 12]. For increasing the used of ginger waste, it processed into oleoresin that incorporated in the paper as an antimicrobial agent. Ginger pulp still contains high oleoresin that have an active compound for antimicrobial activity [1].

Several factors affected the active paper packaging characteristics such as chemical mechanism, storage and distribution condition, physical condition and mechanical properties of packages, sensory properties, and toxicity antimicrobial properties. This research purposed to characterized the physical (thickness, tensile strength, and folding endurance, moisture content), sensory characteristics and antimicrobial activity of active paper by adding ginger pulp oleoresin. Then selected active paper characterized the chemical characteristic by FTIR and compared with active paper no oleoresin.

2. Methodology
2.1. Ginger Pulp Oleoresin Preparation
The ginger pulp was air dried for 8 days until the water content decreased to 12-14%. Dried ginger pulp was milled and sieved to 30 mesh. The pulp was extracted by batch maceration and stirred at 500 rpm. 100-gram ginger pulp (30 mesh) and 600 ml ethanol 96% were mixed and stirred for 2 h at ambient condition, and settled for 12 h at ambient condition and filtered. The ginger pulp extract was evaporated by rotary evaporator RE-300 at 50 °C for oleoresin production [1].

2.2. Active Paper Preparation
15 g of piece filter paper (2 mm x 2 mm) was soaked for 24 h in 250 ml of distilled water. For pulping, the soaked paper and 250 ml distilled water blended in crusher-blender for 5 minutes. The mixture added with tapioca 4.5g/50 ml distilled water and crushed and blended for 5 minutes. 0.45 gram of chitosan in 100 ml acetic acid 1% added, crushed and blended for 5 minutes. Oleoresin emulsion prepared by mixed ginger pulp oleoresin (2%, 4%, and 6%) in 50 ml distilled water while added with tween 80 (1:1) until emulsion formed by stirred. Whereas one sample no added oleoresin used as a control. Pulp, chitosan, and oleoresin emulsion mixed and blended for 5 minutes. The last pulping process was poured into molding paper with screener (20 cm x 30 cm), trimmed, rolled and pressed into wet paper sheet formed. The sheet is dried for 48 h at ambient temperature (30-33 ⁰C).

2.3. Physical Properties of Paper
The moisture content of the active paper was evaluated in the oven at 105 °C for 24 h. The thickness of the active paper was measured by Krisbow micrometer (0.01 mm of precision) [SNI 14-4977-1999]. Tensile strength was measured by Tensile Tester - Kao Tieh (Model KT-7010-A2). Whereas for analysis Tensile strength testing specimen strips were 15 mm wide and 200 mm length. Then both of tip (top and bottom) was clipped within 180 mm by a tensile tester. Run the motor until stop and the sample broken.
The tensile strength value can read directly at SNI 14-0437-1989. Folding endurance was measured by MIT Folding Endurance Tester. For preparation, the strips with a width of 15 ± 0.02 mm and a length of 150 mm are used for the test. The surfaces forming the slot in the folding head have a radius of 0.38 ± 0.02 mm. The clamp oscillates with 175 ± 25 double folds/min through an angle of 135 ± 2° in each direction. Whenever possible a tension of 0.5 kgf shall be used. Record the number of double folds required to sever the specimen (SNI 0491:2009).

2.4. Antimicrobial Test
NA medium (Merck) were used for the growth *P. fluorescens* and PDA medium (Merck) was used for the growth of *A. niger*. *P. fluorescens* was inoculated on nutrient agar for 24 hours. Bacterial cells were ordered to obtain a cell concentration around 10⁶ cells/ml. *A. niger* spores of 7-day cultures were harvested with sterile distilled water with 0.2% Tween 80 (v/v). The concentration of the conidia suspensions was determined using a hemocytometer with an optical microscope at 400 magnification, and 10³ spores were inoculated in the center of the Petri dish for antimicrobial testing. Small paper discs (5 mm diameter) were used for the inhibition zone test. These discs were pre-sterilized non-thermally by keeping the ultraviolet lamp at a distance of 0.5 m for 5–6 h. Active papers containing a various concentration of ginger pulp oleoresin were tested in order to assess their antimicrobial activity. The discs were put on the lid of inoculated Petri dishes. The Petri dishes were incubated 24 h at 37 °C for the growth of *P. fluorescens* and 3 days at 37 °C for the growth of *A. niger*.

2.5. Sensory Properties
Sensory analysis performed by 30 untrained panelists used hedonic test included color, texture, flavor and overall.

2.6. Chemical Properties
The samples have been jarred and KBr-pelleted. The measurements, made on an IR spectrometer Nicolet/Avatar-360 plus device, have been processed with the Spectra Manager.

2.7. Statistical Analysis
SPSS (SPSS 16.0 for Windows) statistical software was used to calculate the analysis of variance (ANOVA) and Duncan Multiple Range Test (DMRT) was used for the comparison of means, with significance assigned at P<0.05.

3. Result And Discussion
The features of the package which make these materials suitable for packaging relate to appearance and performance. Appearance relates the visual impact as color, smoothness, and glossing. Whereas performance properties are related to the level of efficiency achieved during the manufacture of the pack, as stiffness, rigidity strength, tensile strength, wet strength, tear strength, fold endurance moisture content, air permeability, water absorbency, surface friction, surface tension, etc. [13].
Table 1. Physical Properties of Active Paper Packaging

| Oleoresin Concentration | Water Content (%) | Thickness (mm) | Tensile Strength (N/mm) | Folding Endurance |
|-------------------------|-------------------|---------------|------------------------|-------------------|
| 0%                      | 11.11± 2.19       | 0.82± 0.03    | 1.66± 0.20              | 0.48              |
| 2%                      | 9.93± 0.30        | 0.81± 0.00    | 0.54± 0.04              | 0.30              |
| 4%                      | 11.60± 0.13       | 0.77± 0.05    | 0.41± 0.09              | 0.12              |
| 6%                      | 11.86± 1.01       | 0.75± 0.01    | 0.56± 0.13              | 0.30              |

Note: the numbers that are followed by the same letter in the same column and row is insignificantly different based on DMRT test. α= 0.05.

Based on Table 1 the oleoresin variation concentration has no significant effect on the water content of active papers (P\textsubscript{value} > 0.05). However, the water content decreased on incorporated 2% ginger pulp oleoresin (9.93%), then increased to oleoresin addition. The desired water content of the paper is between 4%-8% [14]. In this study, the water content of active papers more than was desired which are 9-11%. In preparation step, the active paper was added to chitosan and oleoresin emulsion that caused water content more than the reference. Chitosan was hygroscopic and have a greater capability to form hydrogen bonding [15, 16]. The presence of Tween 80 emulsifier in the chitosan film increased hygroscopicity due to its hydrophilic groups [16]. The oleoresin variation concentration has no significant effect on the thickness of active paper (P\textsubscript{value} > 0.05). The thickness of active paper about 0.75-0.82 mm. The tensile strength of active papers added with oleoresin were significantly lower than no oleoresin (P\textsubscript{value} < 0.05) (Table 1). Oregano oil enrichment on chitosan film also decreased the tensile strength [17]. The higher of oil content could be attributed to the discontinuities induced in the chitosan matrix by oil droplets which caused a loss of the film cohesion and mechanical resistance [18]. Furthermore, the increasing of water content caused decreasing of tensile strength. The moisture of paper-based packaging materials is mainly due to the development of hydrogen bonds between hydrophilic hydroxyl groups of cellulose fiber in the paper matrix and water molecules replacing the fiber-fiber interaction. Consequently, reducing the intermolecular interaction between fibers [19].

Folding endurance decreased during oleoresin addition (Table 1). Factor influenced the folding endurance were gram s mature, temperature, water content, and structure of paper sheet. Fellers [20] reported that the increasing of grams mature caused the increasing of folding endurance. While, at the same grams mature, the increasing of thickness increased at high flexibility paper caused the increasing of folding endurance.

Table 2. Antimicrobial Activity of Active Paper Packaging

| Oleoresin Concentration | Inhibition Zone (mm) | P. fluorescens | A. niger |
|-------------------------|----------------------|----------------|---------|
| 0%                      | 6.73± 0.053          | 21.91± 2.249   |         |
| 2%                      | 8.43± 0.773          | 27.86± 3.182   |         |
| 4%                      | 8.37± 0.212          | 16.55± 1.184   |         |
| 6%                      | 8.57± 0.188          | 13.74± 6.227   |         |

Note: the numbers that are followed by the same letter in the same column and row is insignificantly different based on DMRT test. α= 0.05.

Active paper incorporated by ginger pulp oleoresin could inhibit bacterial and fungal growth (Table 2). Inhibition zone on P. fluorescens growth by the active paper were affected by the concentration of oleoresin (P\textsubscript{value} < 0.05) while those on A. niger were no affected (P\textsubscript{value} > 0.05).
fluorescent about 6.73-8.57 mm (moderate response, inhibition zone 6-11 mm). Whereas inhibition zone of A. niger about 13.74-27.86 mm (strong inhibition, inhibition zone >11 mm). Elgayar et al [21], classified inhibition zone of tested essential oil were strongly active (inhibition zone, > 11 mm), moderately active (inhibition zone, 6-11 mm), and inactive (no inhibition zone, < 6). Inhibition zone of P. fluorescence is increased with the addition of oleoresin. Antimicrobial activity of control paper due to the nature of chitosan acetate. There were interactions between positively charged chitosan and negatively charged microbial cell wall leads to the leakage of the intracellular constituents [22].

Inhibition zone of P. fluorescence increased at 2% of ginger pulp oleoresin incorporation. In study Nurlaili [1], found 37.13% of zingiberene as antimicrobial. Antifungal activity of active paper about A. niger increased at 2% of ginger pulp oleoresin incorporation but decreased along oleoresin incorporated. Increasing of inhibition zone caused by the antimicrobial activity of chitosan enriched ginger pulp oleoresin incorporated in active paper. Oxygen compound of ginger was electronegative, and hydrocarbon compound (sesquiterpene or monoterpene) that have double bound so showed antimicrobial activity [23]. Whereas decreasing of inhibition zone caused by an emulsion of oleoresin incorporated strongly so active compound diffusion difficulty [24].

Table 3. Hedonic Test of Active Paper Packaging

| Oleoresin Concentration | Parameter  | Color | Flavor | Texture | Overall |
|------------------------|------------|-------|--------|---------|---------|
| 0%                     |            | 4.38  | 3.28   | 3.62    | 3.86    |
| 2%                     |            | 3.86  | 3.41   | 3.00    | 3.41    |
| 4%                     |            | 3.72  | 3.41   | 3.07    | 3.52    |
| 6%                     |            | 3.41  | 3.41   | 2.93    | 3.34    |

Note: the numbers that are followed by the same letter in the same column and row is insignificantly different based on DMRT test. α= 0.05.

Note of score:
1: really dislike, 2: dislike; 3: neutral; 4: like, 5: really like.

An active paper by oleoresin incorporated decreased preference level except parameter of flavor (Table 3). The color of active paper with oleoresin preference level decreased caused dark brown of oleoresin made active paper turbidity than active paper no oleoresin. In parameter texture decreased caused higher of oil content in oleoresin loss of the film cohesion and mechanical resistance.

Table 4. Active Paper Vibration on Specific Wave Number (cm⁻¹)

| No. | Active paper (0%) | Active paper (2%) | Functional group |
|-----|-------------------|-------------------|-----------------|
| 1.  | 3448.87           | -                 | OH              |
| 2.  | -                 | 3422              | OH Fenolic      |
| 3.  | 2902.03           | 2902.03           | CH alkane and OH carboxyclic |
| 4.  | 1633.78           | 1637.64           | N-H (amine)     |
| 5.  | 1429.31           | 1431.24           | C-C aromatic    |
| 6.  | 1372.41           | 1372.41           | C-H alkane      |
| 7.  | 1319.37-1030.03   | 1319.37-1057.04  | C-O dan C-N (aliphatic amine) |
| 8.  | 895.97-661.61     | 897.9-665.47      | C-H aromatic, N-H (amine primer and secondary) |
Figure 1 showed the peaks of cellulose spectrum, a derivative of cellulose and chitosan. Fibre of pine composed of cellulose found at 1160 cm\(^{-1}\), 1316 cm\(^{-1}\), 1370 cm\(^{-1}\) and 1424 cm\(^{-1}\) of wave number and xylan at 1734 cm\(^{-1}\), 1460 cm\(^{-1}\) and 1240 cm\(^{-1}\) of wave number. Those wave number indicated as valency vibration of C-O, C-H, and C-C that related to cellulose and xylan [25]. Active paper has wave number 1163.13 and 1164.09 cm\(^{-1}\); 1319.37 cm\(^{-1}\); 1372.41 cm\(^{-1}\); 1429.31 cm\(^{-1}\), and 1240 and 1241.25 cm\(^{-1}\) were valency vibration to C-O, C-H and C-C that related to cellulose. In the study, also found acetyl group at (1319.37-1030.03) cm\(^{-1}\), hydroxyl group at 3448.87 cm\(^{-1}\) and amine primer (1633.78 dan 1637.64) cm\(^{-1}\). There was the structure of chitosan acetate. The ginger compound also found in active paper selected sample with wave number about 3379-3422 cm\(^{-1}\) and identified as valence vibrations corresponding to the OH groups of red ginger [26].

4. Conclusion

Active paper with ginger pulp oleoresin reduced tensile strength, folding endurance and sensory characteristic (color, texture and overall) and increased antibacterial activity but antifungal activity decreased. Due to physical, chemical, sensory characteristic and microbial activity, active paper with 2% ginger pulp oleoresin incorporation was selected. Characteristics of selected paper were 9.93% of water content; 0.81 mm of thickness; 0.54 N / mm tensile strength; 0.30 of folding endurance; 8.43 mm inhibits the growth of \textit{P. fluorescent}, and 27.86 mm inhibits the growth of \textit{A. niger} (antimicrobial activity) and neutral preference response for sensory properties. Chemical properties found O-H group of red ginger active compound.

Acknowledgements

This work was financially supported by a research project of PNBP No: 698/UN27/ PN/2015 from Sebelas Maret University, Indonesia.
References

[1] Nurlaili F A, Darmadji P and Pranoto Y 2014 Microencapsulation of Pulp Ginger (Zingiber officinale var. Rubrum) Oleoresin with Maltodextrin Coating AGRITECH 34 1 p 23 27

[2] Gaedcke F and Bjorn F 2005 Ginger Extract Preparation US Patent Application Publication US 2005/0031772 A1

[3] Brody A L, Strupinsky E R and Kline L R 2001 Active Packaging for Food Application CRC Press USA

[4] Balasubramanian A, Rosenberg L L E, Yam K and Chikindas M L 2009 Antimicrobial Packaging: Potential vs. Reality—A Review Journal of Applied Packaging Research. 3 4 p 195

[5] Suppakul P, Miltz J, Sonneveld J, and Bigger S W 2003 Active Packaging Technologies with an Emphasis on Antimicrobial Packaging and its Applications Journal of Food Science 68 2 p 411

[6] Opara U L and Mditchwa A 2013 A Review of The Role of Packaging in Securing Food System: Adding Value to Food Products and Reducing Losses and Waste African Journal of Agricultural Research. 8 22 p 2622

[7] Rakchoy S, Suppakul P and Jiankarn T 2009 Antimicrobial Effects Of Vanillin Coated Solution for Coating Paperboard Intended for Packaging Bakery Products As. J. Food Ag-Ind. 2 4 p 139

[8] Stoyanova A, Denkova Z, Noven N, Slavehev A, Jirovetz L, Buchbauer G, Lien H N, Schimidt E and Geissler M 2007 C2H2F2-SCFE-Oleoresins of Black Pepper (Piper Nigrum L.) and Ginger (Zingiber officinale (L.) Rosc.) from Vietnam: Antimicrobial Testings Gas Chromatographic Analysis and Olfactoric Evaluation Electron. J Environ Agric Food Chem 5 5 p 1617-1618

[9] Mikusansanti H and Masril K I 2013 Antibacterial and Antioxidant of Uwi (Dioscorea Alata L) Starch Edible Film Incorporated with Ginger Essential Oil International Journal of Bioscience Biochemistry and Biopharmaceutics 3 4 p 355

[10] Barman K L and Jha D K 2013 Comparative Chemical Constituents and Antimicrobial Activity of Normal and Organic Ginger Oils (Zingiber officinale roscoe) International Journal of Applied Biology and Pharmaceutical Technology 4 1 p 263

[11] Supreetha Sharadadevi M, Sequira P S, Jithesh J, Shreyas T and Amit M 2011 Antifungal Activity of GingerExtract on Candida Albicans: An In-vitro Study Journal of Dental Science and Research 2 2 p 20

[12] Sabra S M M, Al-Masoudi L M R, Al-Gehani S A H and Harbaha A A O A 2014 Comparative Laboratory Study on Antimicrobial Effects of Fresh and Dry Ginger (Zingiber officinale) Taif KSA IOSR-JESTFT 8 9 p 119

[13] Coles R, McDowell D and Kirwan M J 2003 Food Packaging Technology Blackwell Publishing Ltd. UK

[14] Li PY, Ramaswamy S and Bjegovic P 2003 Pre-emptive Control of Moisture Content in Paper Manufacturing Using Surrogate Measurements Transactions of The Institute of Measurement and Control. 25 1 p 40

[15] Szymańska E and Winnicka K 2015 Stability of Chitosan—A Challenge for Pharmaceutical and Biomedical Applications Mar. Drugs. 2015 13 p 1827

[16] Muresan A, Cerempai A, Dunca S, Muresan R and Butnaru R 2009 Aromatherapeutic Characteristics of Cotton Fabrics Treated With Rosemary Essential Oil. Cellulose Chem.Technol. 43 9-10 p 440

[17] Chi S 2004 Development and Characterization of Antimicrobial Food Coatings Based on Chitosan and Essential Oils Thesis University of Tennessee Knoxville
[18] Bonilla J, M Vargas L Atares and A Chiralt 2011 Physical properties of chitosan-basil essential oil edible films as affected by oil content and homogenization conditions Procedia Food Science 1 2011 p 53

[19] Rhim J W 2010 Effect of Moisture Content on Tensile Properties of Paper-based Food Packaging Material Food Sci. Biotechnol. 19 1 p 245-246

[20] Feller C, Iversen T, Linndstrom T, Nilsson T and Rigidal M 1989 Ageing/Degradation of Paper ISSN 0284-5636 Stockholm

[21] Elgayyar M, F A Draughon, D A Golden and J R Mount. 2001 Antimicrobial Activity of Essential Oils from Plants against Selected Pathogenic and Saprophytic Microorganisms Journal of Food Protection 64 7 p 1019

[22] Huang L, Dai T, Xuan Y, Tegos G P and Hamblin M R 2011 Synergistic Combination of Chitosan Acetate with Nanoparticle Silver as a Topical Antimicrobial: Efficacy against Bacterial Burn Infections Antimicrob Agents Chemother 55 7 p 3432-34338

[23] Sasidharan I and A N Menon 2010 Comparative Chemical Composition and Antimicrobial Activity Fresh and Dry Ginger Oil (Zingiber officinale rosco) Int. J Curr Pharm Res 2 4 p 42

[24] Maleki S, S M Seyyednejad, N M Damabi and H Motamedi 2008 Antibacterial Activity of The Fruits of Iranian Torilis leptophylla Against Some Clinical Pathogens Pakistan Journal of Biological Sciences 11 9 p 1286-1289

[25] Fan M, D Dai and B Huang 2012 Fourier Transform-Material Analysis Intech Europe

[26] Purwakusumah E Dj, M Rafi, U D Syafitri, W Nurcholis dan M A Z Adzkiya 2014 Identification and Authentication of Jahe Merah Using Combination of FTIR Spectroscopy and Chemometrics AGRITECH 34 1 p 83-84