Changes in grammage, tearing resistance, and water vapor transmission rate of active paper incorporated with Cinnamaldehyde during storage at various temperatures

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Abstract. Antimicrobial properties of active paper packaging incorporated with cinnamaldehyde and its application in the storage of agricultural products had been studied. However, changes in grammage, tear resistance and water vapor transmission rate (WVTR) of the active paper during storage is not yet known, whereas it is important to provide consideration in application of the active paper. This study aims to determine the changes in those physical properties during storage (20 days) at various temperatures (10, 20, 25, 30, and 40 °C). The grammage and WVTR of the active paper decreased as increase in storage time and temperature, while the tearing resistance increased as storage time. Higher temperature caused slower increase in tearing resistance, but the results showed fluctuation. The results of Arrhenius plot indicated the activation energy (in kJ/mol) of those physical properties, sorted from the highest to the lowest as follows: 53.6 (grammage), 14.8 (WVTR) and 13.8 (tearing resistance).

1. Introduction
Paper has undergone many developments of its raw materials and application. Fibers from papyrus stems were used as raw material for paper in the kingdom of Ancient Egypt, then the Chinese people used paper for food packaging in the first or second century BC. Modern society has used paper container that is flexible or rigid, as well as coated or mixed with other packaging materials such as plastic and metal foils to improve its function and properties [1, 2]. Paper made from pulp, that was coated or mixed with a chitosan to enhance its barrier properties against oxygen, carbon dioxide, nitrogen, air and water had also been widely studied [2, 3, 4]. Moreover, recently, the paper with addition of active materials such as cinnamon bark essential oil or cinnamaldehyde (a major compound in cinnamon bark essential oil) had been developed to produce active paper with effective inhibition to microbial growth and deterioration of fresh fruit such as tomatoes, cherries, strawberries, and rambutans [5, 6, 7, 8]. Paper-based active packaging was also reportedly more effective in growth inhibition of bacteria rather than film-based active packaging [9].

However, research on active packaging is still focused on the effect of active material concentration to the antimicrobial activity, and physical properties such as tensile resistance, elastic modulus, elongation, microtopography surface as well as controlled release mechanism of the active materials [10, 11, 12, 13, 14]. Degradation or changes in physical properties of paper-based active packaging during storage have never been investigated.
So far, degradation of ordinary paper (not active paper) during storage had been widely studied, but the studies treated the paper at very high temperature (≥80 °C). The experiment at lower temperatures or close to normal storage temperature was proposed to predict, more accurately, the changes of the paper. This method employed Arrhenius-plot with the slope giving an apparent activation energy which represent minimal energy required for a reaction to take place [15].

Thus, this study was designed to investigate changes in physical properties (grammage, water vapor transmission rate, and tearing resistance) of active paper made from pulp and chitosan incorporated with cinnamaldehyde during storage at various temperatures (10, 20, 25, 30 and 40 °C). It is necessary to study those properties because grammage affects other physical properties, while the water vapor transmission rate (WVTR) and tearing resistance affect active paper application, especially when it is used in agricultural product storage. Finally, the activation energy of each physical properties is analyzed so that the most susceptible property of active paper to change during storage can be determined.

2. Materials and Methods

2.1. Materials

Materials used for the preparation of the active paper is cinnamaldehyde with 99.99% purity (supplied from Aldrich), kraft paper, chitosan (from local supplier/ Chemix Pratama), and acetic acid (from Merck).

2.2. Methods

2.2.1. Preparation of active paper. The active paper was made from the mixture of pulp and chitosan incorporated with cinnamaldehyde. At first, three kinds of ingredients was prepared. They were pulp, solution of chitosan in acetic acid, and cinnamaldehyde emulsion in distilled water. Pieces of kraft paper (dimension about 2 mm x 2 mm; 6%w/v) were soaked in distilled water for 24 hours then beaten in a blender for 5 minutes into pulp. Chitosan powder (0.45%w/v) was dissolved into a solution of 1% acetic acid. In a separate beaker glass, tween-80 (0.45%w/v) was dissolved in distilled water. Cinnamaldehyde (2.5%w/w of kraft paper) was added to the emulsion of tween-80, then it was constantly stirred for 5 minutes to produce cinnamaldehyde emulsion. These three ingredients were slowly mixed in blender for 5 minutes, then evenly poured onto the filter surface in the cast (20 cm x 20 cm) until rough sheet of wet paper was formed. The sheet on filter was then compressed under glass plate with 2.0 kg load for 10 minutes to remove residual water. The sheets were dried at 30 °C for 48 hours and flipped after the first 24 hours of drying.

2.2.2. Storage of active paper. The paper sheets (20 cm x 30 cm) were stored by hanging on a hanger rod made of glass (to avoid migration of compounds from the hanger into the paper) in incubator box with temperature variation of 10, 20, 25, 30, and 40 °C for 20 days. Every 5 days, samples of each temperature were taken to be analyzed for its grammage, water vapor transmission rate (WVTR), and tearing resistance.

2.2.3. Grammage. Grammage test method of paper and paperboard according Indonesia National Standard test (SNI 14-0439-1989) was employed as follows. Paper samples were taken with the size of 10 cm x 10 cm. Grammage (in g/m²) was then determined by weighing the sample material and dividing the weight by the area.

2.2.4. Water vapor transmission rate (WVTR). The measurement of water vapor transmission rate was performed based on ASTM E096-95 as follows. Paper samples were cut in the shape of a circle. Three test dishes were filled with distilled water up to a level 19 ± 6 mm from the paper samples. The
specimens were then attached to the dish. The dishes were then assembled and placed on a true horizontal surface in a chamber. The chamber humidity and temperature must be controlled at 90% relative humidity and 38 °C. The dishes were weighed periodically (every 3 hours) for 24 hours and recorded by automatic device attached to the horizontal surface. The weight then was plotted into a graph against elapsed time, in order to obtain a curve which tends to become straight. WVTR (in g/m².h) was then calculated by dividing the slope of straight line by the test area (cup mouth area).

2.2.5. Tearing resistance. Tearing resistance measurement was performed based on Elmendorf-type method from SNI (Indonesia National Standard) 0436:2009 which refer to TAPPI (Technical Association for the Pulp and Paper Industry) 414 om-04 and ISO 1974:1990. Samples of paper were clipped vertically on the tool. The test was performed by inducing a crack in the test piece and applying a load perpendicular to the face to pull the paper apart. The pendulum was released to swing freely and tear the paper, then the value indicated by the pointer was recorded as tearing resistance (in mN).

2.2.6. Activation energy. The activation energy was determined by using the Arrhenius-type plot based on the results of grammage, WVTR, and tearing resistance test. Paper storage time (0, 5, 10, 15, 20) was plotted on the horizontal axis, while the physical properties (grammage, WVTR, or tear resistance) was plotted on the vertical axis for the first order or natural logarithmic of the physical properties on the vertical axis, so that slope obtained for each storage temperature (10, 20, 25, 30, and 40 °C). The next curve is made using natural logarithmic slope of the slope on the vertical axis and inversion of the absolute temperature (K⁻¹) on the horizontal axis to produce a slope (Ea/ R) giving an activation energy (Ea).

3. Result and Discussion

3.1. Rammage
The active paper grammage decreased during 20 days of storage (Figure 1). Higher temperature resulted in more rapid decrease of the grammage. Thus, the most rapid decrease in grammage was demonstrated by the active paper stored at 40 °C, while the slowest one was demonstrated by the active paper stored at 10 °C. The decrease of grammage might be associated with moisture content of the active paper that also decreased more rapid as the storage temperature (the data not shown).

The grammage of the active paper was five to six times higher than commercial kraft paper grammage and three to four times higher than the paper made from pulp-chitosan resulted from other studies [2, 16]. Additional material (such as chitosan, tween-80, and cinnamaldehyde) and higher amount of total material used resulted in the striking difference. The active paper grammage met ISO standards for paperboard or slightly below the standard. Grammage affected tensile strength as well as dewatering and rewetting of paper based on the other studies [17, 18].

3.2. Water vapor transmission rate
Water vapor transmission rate (WVTR) of active paper decreased during 20 days of storage (Figure 2). Higher storage temperature resulted in more rapid decrease of WVTR. The most rapid decrease in WVTR was demonstrated by the active paper stored at 40 °C, while the slowest one was demonstrated by the active paper stored at 10 °C. Lower WVTR of indicates that the paper or film layer is more difficult to be passed through by water vapor.

The decrease of WVTR may be associated with moisture content of the active paper that also decreased more rapid as the temperature increase. Other study indicated that the moisture content affected the formation of more porous polymer network structure in the film [19]. The loss of water molecules from the active paper during storage or due to higher temperature might result in more dense structure of polymer chains (both cellulose and chitosan) and more intermolecular interactions, eg hydrogen bonds. The other studies also reported the formation of more solid structure due to higher
temperatures employed in the film preparation [20, 21]. Higher density was also associated with lower air permeance of paper [16]. Thus, increased density of the active paper as the increased temperature and time of storage might result in the decrease of WVTR.

![Figure 1. Grammage of paper](image1)

![Figure 2. WVTR of paper](image2)

### Table 1. Activation energy of active paper physical properties

| Physical properties | Activation energy (kJ/mol) |
|---------------------|---------------------------|
| Grammage            | 53.6                      |
| WVTR                | 14.8                      |
| Tearing resistance  | 13.8                      |

3.3. Tearing resistance

Tearing resistance of the active paper increased during storage of 20 days (Figure 3). The result confirmed the increased density of polymer network in the active paper due to the loss of water molecules during storage as indicated by WVTR test result. However, the temperature effect on the rate of increase in the tearing resistance seemed contrary to the temperature effect on the rate of increase in WVTR. Higher temperature resulted in slower increase in tearing resistance, so that the most rapid increase in tearing resistance was demonstrated by the active paper stored at 10 °C, while the slowest increase in tearing resistance was demonstrated by the active paper stored at 40 °C. The result led to speculation that other factor might affect tearing resistance in addition to the density of the polymer network structure or paper moisture content.

The slower increase in tearing resistance at the higher temperature might be associated with the negative effect of paper degradation which was more intense at the higher temperature. Initially, paper degradation begin with polymer chain scission in the amorphous region and continued with the formation of crosslinks between polymers, which led to increased brittleness and decreased tearing resistance [16, 22]. Thus, this result raised other speculation that the paper polymers degradation due to higher temperature only affected tearing resistance, but had no effect on WVTR. It would need further study and comparison. So far, the studies on the temperature effect on the paper degradation focused on folding endurance and tensile resistance [23, 24], while tearing resistance and WVTR never been studied.
3.4. Activation energy
The activation energy indicates the amount of energy required to initiate the reaction or changes in particular material. The study of the activation energy has been commonly used for food deterioration and cooking as well as chemical reactions based on Arrhenius plot [25, 26]. However, so far, the studies of paper degradation during storage employed one or two high temperature (≥80 °C) at various humidity. Lately, the method is doubtful because the experimental design does not reflect normal storage conditions so that it might lead to wrong conclusion [15, 22]. Therefore, this study employed storage temperature of 10, 20, 25, 30, and 40 °C to provide the better representation of the physical changes that might occur in the active paper. The changes might involve particular chemical reaction in the active paper. The activation energy for the physical properties of the active paper presented in (Table 1).

The result indicated that the paper strength was sensitive to changes during storage. The tearing resistance was the most susceptible properties to be affected during storage. However, the tearing resistance demonstrated increased trend, while the decrease was noted in grammage and WVTR. As discussed earlier, increased tearing resistance due to temperature and storage might be associated with decreased moisture content that result in increased density of the paper materials. It means that the effect of density or moisture content of the paper was greater than the paper degradation. Nevertheless, further research on changes in other physical properties of the active paper such as folding endurance and tensile resistance is needed to confirm this result.

4. Conclusion
The grammage and WVTR of active paper decreased as increased storage time and temperature, while the tearing resistance increased during storage. Higher temperature caused more rapid decrease in the grammage and WVTR, but slower increase in the tearing resistance during storage. The activation energy sorted from the highest to the lowest as follows: grammage, WVTR, and tearing resistance. Therefore, the tearing resistance was the most sensitive properties of the active paper.

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