The Study on Chitosan Coating on Poly(Lactic Acid) Film Packaging to Extend Vegetable and Fruit Life

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Abstract. The objective of this work is the study of possibility of extending the life of vegetables and fruits packed with polyactic acid (PLA) film coated with squid chitosan with various contents (0, 1, 3 and 5 phr), acted as an antimicrobial agent and the study of mechanical properties of these films. In the first step, PLA was compounded with 20 percents of glycerol by using a two-roll mill. After that, all compounds were fabricated by blown film extrusion. In next step, the chitosan solutions were prepared in 1 wt% hydrochloric acid solution to coat on one side of PLA film. The last step, the prepared films were examined tensile properties and storage time of 4 types of vegetables and fruits including broccolis, Leb Mue Nang bananas, red grapes and queen tomatoes by packing. The results showed that the tensile strength of PLA films coated with chitosan was closed to that of neat PLA/glycerol film. For spoilage test, it was found that all vegetables and fruits were more shriveled and wilted with more chitosan content through respiration process due to the leakage of chitosan coated PLA film and weight loss of vegetables and fruits., especially for PLA film coated with 5 phr chitosan since more remained acetic acid solvent accelerated more hydrolysis rate of PLA film.

1. Introduction

One of environmental concerns for all countries in the world is a reduction of marine animals caused from litter of oil-based plastic which cannot be biodegraded, especially food packaging plastic. After many marine and wild animals were killed by plastic waste in Thailand, Thai government issued policies to reduce plastic waste problems as they are aware of the increasing volume of plastic waste and its negative environmental effects \cite{1}. Several local plastic resin producers in Thailand e.g. PTTGC, Total Corbion PLA initiate plan to build polyactic acid (PLA) plant for compostable packaging that is a solution that uniquely fits Thailand’s waste management infrastructure \cite{2}. However, adoption rate of PLA for food packaging in Thailand by packaging manufacturers and brand owners is gradually decreasing because of its limited applicability and function/performance-to-cost ratio. For example, PLA has limited applicability to fabricate packaging film for short shelf-life products due to its brittleness and high water vapor permeability. Thus, blending of low-cost biodegradable polymers or additives to develop functional attribute and performance to PLA but still maintaining its compostability with reasonable cost is demanding to promote bioplastic adoption and replace conventional plastic for food packaging \cite{3, 4}. Rong Zhang \textit{et al.} \cite{5} researched the blending of poly (butylene adipate-co-terephthalate) (PBAT) in PLA films to preserve quality of passion fruits during shelf-life. Their results were found that PLA/PBAT film can retard the metabolism of passion fruits, reduce weight loss, shrinkage index, firmness, total sugar, total acid, ascorbic acid content,
ethanol content, sensory evaluation, and aroma components compared with PE film. However, in contrast to PE, both PLA and PBT were biodegradable polymers. Furthermore, chitosan is one of the bio-derived and biodegradable additives that is widely used as functional additive for plastic packaging. Due to its antimicrobial properties and permeability-reducing properties [6], it has potential to extend shelf-life of vegetable and fruit products. Chitosan is derivative of chitin, which is amino polysaccharide and basically found in shell of crab, lobster, shrimp, insect and squid [7]. In 2013, Irkin R and Guldas M [8] have studied antimicrobial action of chitosan on fungal in red grape and honey melon samples. They found that chitosan coating on red grape and honey melon successfully inhibits fungi (Fusarium oxysporum) growth. Another study, Sanga S and Hongsriphan N [9] prepared antibacterial food packaging films from 90/10 wt% of PLA/PBS by dip coating of chitosan solution on films. Corona treatment was applied on film surface before chitosan coating to improve the adsorption of chitosan. The obtained films revealed higher antibacterial activity against E.coli and S.aureus, with higher chitosan concentration. However, chitosan prepared by low-cost process has not been investigated.

This current research work aimed to investigate the applicability of α-chitosan from squid pen in PLA packaging film to extend shelf-life of vegetable and fruit products and also aimed to characterize the tensile properties of PLA biofilm with chitosan bio-additive to become an alternative to a single-use plastic packaging.

2. Experimental

2.1. Materials
Polyactic acid pellet (PLA), (Ingeo™ 4043D, MFI of 6 g/10 min at 210°C/ 2.16 kg.) was supplied by, NatureWork LLC, USA). High molecular weight α-chitosan powder from squid pen (food grade, particle size 18 mesh, viscosity > 1,000 Cps, degree of deacetylation >95%) was supplied by Bona Fides Marketing co., ltd. (Bangkok, Thailand). Glacial acetic acid (99.5% purity) was purchased from SNP General Trading co., ltd. (Bangkok, Thailand). And glycerol (99.5% purity) was purchased from Lab Valley LP. (Bangkok, Thailand). For the spoilage study, broccolis, Leb Mue Nang bananas, red grapes, and queen tomatoes were purchased in a local supermarket. All chemicals were used without further purification.

2.2. Compounding and film processing
Before compounding, PLA pellets and glycerol were premixed by manually stirring in beaker with a PLA/glycerol ratio of 80/20wt%. Then, they were dried at 60°C in an air-circulating oven for 24 h in order to remove moisture. The mixture of PLA and glycerol were compounded by two-roll mill at 180°C for 15 min. PLA compound was cooled at room temperature and granulated by cutter grinder. The film-forming process was carried out by blown film extruder with a screw speed of 60 rpm, nip roll speed of 4.0 m/min, winding speed of 4.2 m/min, internal bubble cooling speed of 1600 rpm and temperature profile ranging from 160°C to 180°C. Film thickness was measured using a micrometer.

2.3. Chitosan coating on PLA films
PLA film was cut in glass mold size (20 cm x 30 cm) and then weighted to determine the required amount of chitosan. Chitosan powder with various amounts (1, 3 and 5 phr of sized PLA film) was dissolved in a 30 ml of 1wt% acetic acid with continuous stirring at room temperature until solution was clear. Chitosan solution was poured onto PLA film mounted on glass mold. Chitosan coated PLA film was left at room temperature for 3 days to evaporate acetic acid and was then removed from glass mold for further testing. Thus, the single side chitosan coated PLA film was obtained.

2.4. Characterization and Testing
2.4.1. Tensile testing. Prepared films of pure PLA (with glycerol), PLA/1 phr chitosan, PLA/3 phr chitosan and PLA/5 phr chitosan were determined tensile properties in accordance to ASTM D882 using a Universal Testing Machine (Testometric, Model M500-25AT) in both machine direction (MD)
and transverse direction (TD). The samples were tensioned with a crosshead speed of 50 mm/min using load cell of 100 N.

2.4.2. Spoilage testing. The broccolis, Leb Mue Nang bananas, red grapes, and queen tomatoes were separated from clusters and they were packed in sealed PLA film coated with different chitosan concentrations along with chitosan coated side of film was turned inward to expose to vegetables and fruits. Then, they were put on laboratory bench at room temperature for a week. The photos of vegetables and fruits were taken in everyday to observe texture and appearance change and all samples (including vegetable or fruit and PLA film) were weighted to analyze weight loss corresponding to spoilage rate.

3. Results and Discussions

3.1. Tensile properties of PLA film coated with different concentrations of chitosan

Tensile strength, elongation at break and Young’s modulus of both MD and TD of PLA film adding 20wt% of glycerol together with 1, 3 and 5 phr of chitosan by coating were investigated and shown in figure 1. It was found that the tensile properties of uncoated PLA film were very low that might due to the presence of immiscible glycerol in PLA matrix. Compared with coated PLA films, PLA film coated with 1 phr of chitosan presented quite low tensile properties especially for tensile strength and Young’s modulus in MD. This is due to roughness on film surface which was occurred from poor dispersion of low chitosan content resulting in stress concentration that caused easily breaking of films [10]. While, all tensile properties of PLA films coating chitosan of either 3 or 5 phr were not significantly different from that of uncoated film in both film directions. Also the Young’s modulus was slightly increased with chitosan increasing. This was attributed to the rigid cellulosic-like structure of chitosan. Therefore, it did not impact on practical application of the coated film samples compared with uncoated one.

![Figure 1](image)

**Figure 1.** (a) Tensile strength, (b) elongation at break and (c) Young’s modulus of PLA film coated with different chitosan contents in machine direction (MD) and transverse direction (TD).

3.2. Spoilage testing of vegetables and fruits in chitosan coated PLA films

The loss of appearance qualities such as aroma, texture, taste, or color is generally used to describe ‘spoilage of food’. Therefore, the visual appearance including color and texture were carried out to simply considerate the spoilage of studied vegetables and fruits. The visual appearance of broccolis,
Leb Mue Nang bananas, red grapes, and queen tomatoes packed in PLA films packaging of 10 cm x 15 cm in size are presented in figure 2, 3. The figures showed that color of some parts of banana peels became black, broccolis became yellowish, as well as grapes and tomatoes peels were darker when they were left at room temperature for longer time with higher chitosan contents. In addition, a head of broccoli was more shriveled as well as external textures of bananas, red grapes and queen tomatoes were more wilted during 7 days due to water loss causing condensation of water on film surface coated with chitosan. Compared with uncoated PLA film, the film packages were clear and not found water drop on film surface caused by high water vapor permeability of PLA film. In generally, factors of vegetables and fruits spoilage are the physiological age, the storage temperature, the storage atmosphere (humidity) and microorganism presence. This work intended to improve vapor barrier property of PLA and reduce microorganism growth using chitosan coating and the result also revealed that water drop was more occurred when vegetables and fruits were packed in PLA film for longer time with higher chitosan contents. It meant that chitosan coating can protect water permeation but it cannot reduce water loss of vegetables and fruits. Therefore, too high humidity trapped in packaging can aid to fungi growth. However, mold which is a one of fungus species were not appeared on vegetable and fruit samples. These results indicated that chitosan can against microbial attack.

![Image of different chitosan contents for 7 days.](image1)

![Image of different chitosan contents for 7 days.](image2)

![Image of different chitosan contents for 7 days.](image3)

**Figure 2.** Appearance of (a) broccolis, (b) Leb Mue Nang bananas and (c) red grapes packed in PLA film packaging coated with different chitosan contents for 7 days.
Figure 3. Appearance of queen tomatoes packed in PLA film packaging coated with different chitosan contents for 7 days.

Figure 4. Weight loss of (a) broccolis, (b) Leb Mue Nang bananas, (c) red grapes and (d) queen tomatoes packed in PLA film packaging coated with different chitosan contents.

In addition, this work determined the weight loss of vegetables and fruits to evaluate an acceptable quality for marketing and to evidence the metabolism of harvested plants. These results were shown in figure 4, they presented that an increase chitosan increased the weight loss of all vegetables and fruits and the broccoli exhibited the highest rate of weight loss following by bananas, grapes and tomatoes, respectively. Normally, the weight loss was related to respiration and water loss of harvest plants and their rate depended on type of plant, which generally faster in leafy vegetables [11]. As above description, we found water drop were trapped in only chitosan coated PLA film indicating that water were lost from vegetables and fruits but it was not lost from film packaging whereas their weight loss was enhanced with chitosan increasing. This is suggested that the weight loss of vegetables and fruits was caused by respiration which is process that plants take in oxygen to break their carbohydrate into carbon dioxide and water. So, the presence of water drop in chitosan coated PLA film is the product of plant respiration which cannot permeate this film while a small molecule of carbon dioxide can do. This result was in contrast to the uncoated PLA film, the prepared chitosan coated PLA film also had a good water vapor barrier property but it had poor gas barrier property. Therefore, it was possible that
acetic acid solvent was remained after chitosan coating and it induced the leakage of carbon dioxide since acidic sensitivity of PLA caused some hydrolytic degradation [12].

4. Conclusion
Chitosan coated PLA film was prepared by cast coating of squid chitosan on a single side of 80%PLA/20% glycerol films which was an economical simple process. For spoilage test of vegetables and fruits packed in chitosan coated PLA film, it can be concluded that chitosan coating on PLA film can satisfyingly inhibit mold or microorganism growth on vegetables and fruits even high humidity. In addition, both 3 and 5 phr of chitosan did not significantly change the tensile properties of PLA film. However, chitosan coating using casting method also left acetic acid solvent on PLA film, resulting in some hydrolytic degradation of PLA. This result intended to increase respiration rate of vegetables and fruits taking air or oxygen that permeated chitosan coating PLA films. Besides, both water and carbon dioxide were produced from this metabolism which the water was trapped into these films but the carbon dioxide was leaked trough the film leading to shriveling and weight loss of vegetables and fruits. Although both vegetables and fruits were not spoiled by microorganism, they were shiveled and wilting that is unacceptable for sale. In conclusion, chitosan also was a suitable antimicrobial agent for bioplastic package, but alternative coating technique could be considered.

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