Synthesis and Characterization of Silica Hybrid Coating Materials for Poly (lactic acid) Film

Fan Wu

A Thesis Submitted in Fulfillment of the Requirements for the
Degree of Master of Science in Packaging Technology
Prince of Songkla University
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ชื่อวิทยานิพนธ์ การสังเคราะห์และวิเคราะห์วัสดุเคลือบ silica hybrid สำหรับฟิล์มพอลิแลคติกแอซิด

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บทคัดย่อ

วัสดุผสมระหว่างซิลิกากับพอลิแลคติกแอซิด (Silica/poly(lactic acid)) ซึ่งเตรียมได้จากกระบวนการโซลเจล (sol-gel) เพื่อปรับปรุงสมบัติการซึมผ่านออกซิเจนและไอน้ำของฟิล์มพอลิแลคติกแอซิด โดยใช้เตตระเอททอกซีไซเลน (Tetraethoxysilane, TEOS) กับไตรเอททอกซีไวนิลไซเลน (Triethoxyvinylsilane, VTES) ซึ่งมีพันธะคู่ ทำปฏิกิริยาโค-ไฮโดรไลสิส (Co-hydrolysis) และปฏิกิริยาการควบแน่น (Polycondensation) โดยจะเกิดการเชื่อมต่อของพันธะคู่ระหว่างซิลิเกตกับหมู่ไซลอกเซนภายในโครงสร้าง กระบวนการพอลิเมอไรเซชันของพันธะไม่อิ่มตัวเกิดขึ้นได้ด้วยการฉายรังสียูวี ซึ่งสามารถยืนยันได้โดยการลดลงของ FTIR พีคที่ 1600 cm^{-1} แสดงการสั่นแบบยืดของพันธะคู่ (C=C stretching) รวมทั้งการใช้พอลิแลคติกแอซิดและไตรไอโซไซยาเนโตโพรพิลไตรเอททอกซีไซเลน (3-Isocyanatopropyltriethoxysilane, ICPTES) เป็นสารคู่ควบ ทำให้เกิดพีคที่ 1550 cm^{-1} ที่แสดงถึงเอกลักษณ์ของหมู่เอมีน (-NH group) เนื่องจากหมู่ไอโซไซยาเนตใน ICPTES เกิดปฏิกิริยากับหมู่ไฮดรอกซิลในสายโซ่ของพอลิแลคติกแอซิด จากการทดสอบทางสัญฐานวิทยาแสดงให้เห็นถึงรอยแตกที่ผิวหน้าของผิวเคลือบที่ไม่เติม ICPTES การเคลือบผิวฟิล์มพอลิแลคติกแอซิดด้วย VTES/TEOS ในอัตราส่วน 1:1 (VT11) ปรับปรุงสมบัติการต้านการซึมผ่านไอน้ำ 24.6 เปอร์เซ็นต์ ค่าสัมประสิทธิ์การซึมผ่านของออกซิเจนลดลง 24.8 เปอร์เซ็นต์ เมื่อเปรียบเทียบกับฟิล์มพอลิแลคติกแอซิดบริสุทธิ์ นอกจากนี้เมื่อนำฟิล์มพอลิแลคติกแอซิดเคลือบ VT11 มาทำการฉายรังสียูวีเป็นเวลา 1 ชั่วโมง พบว่า มุมสัมผัสของน้ำลดลง 6.6 เปอร์เซ็นต์ ปริมาณผลึกที่เกิดขึ้นน้อยลงและการวิเคราะห์โดยเทคนิค AFM พบว่าความขรุขระของผิวลดลง 31.2 เปอร์เซ็นต์ นอกจากนี้พบว่าเมื่อเวลาในการ aging เพิ่มขึ้นสามารถปรับปรุงสมบัติการต้านการซึมผ่านไอน้ำได้ดีขึ้น เพราะเกิดการเชื่อมโยงของสายโซ่ภายในโครงสร้างที่หนาแน่นขึ้น นอกจากนี้การฉายรังสียูวีให้กับฟิล์มพอลิแลคติกแอซิดเคลือบ VT11 สามารถช่วยชะลอการเกิดปฏิกิริยาออกซิเดชันของไขมันได้ดีกว่าฟิล์ม

พอลิแลคติกแอซิด และฟิล์มพอลิเอทิลีนความหนาแน่นต่ำ (Low density polyethylene, LDPE) ซึ่งฟิล์มพอลิแลคติกแอซิดเคลือบ VT11 จึงเป็นอีกทางเลือกที่สามารถนำไปใช้ในการเก็บรักษาคุณภาพและยืดอายุของข้าวเกรียบกุ้งได้

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Author: Mr. Fan Wu
Major Program: Packaging Technology
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ABSTRACT

Silica/poly(lactic acid) hybrid materials were synthesized by sol-gel method and used as coating materials in order to improve the oxygen and water vapor barrier property of, poly(lactic acid), PLA films. The mixtures of Tetraethoxysilane (TEOS) and Triethoxyvinylsilane (VTES), containing a reactive double bond, were used as the inorganic silicate precursors to construct the siloxane network structure by co-hydrolysis and polycondensation reaction. Polymerization of the unsaturated bonds occurred by UV irradiation, as evidenced by sharp decrease of FTIR band at 1600 cm^{-1}, corresponding to terminal C=C stretching bond. PLA and 3-Isocyanatopropyl-triethoxysilane (ICPTES) were used as an organic polymer and a silane coupling agent, respectively. FTIR absorption band at 1550 cm^{-1} was specified to the formation of amine groups (-NH), due to isocyanate groups in ICPTES reacting with hydroxyl groups in PLA chains. SEM was indicated that there were big cracks on the surface of coating materials without ICPTES. The water vapor barrier property of coated film showed a great improvement by 24.6% at the VTES/ TEOS ratio of 1: 1 (VT11), and the oxygen permeation coefficient (OPC) of VT11-coated film was decreased 24.8%, as compared to PLA neat film. The water contact angle of VT11-coated film decreased by 6.6%. XRD showed that the crystallinity of VT11-coated film was decreased after UV-irradiation for 1h. AFM also indicated that surface roughness of VT11-coated film decreased by 31.2% after UV-irradiation for 1h. Moreover, the water vapor barrier property was improved with the aging time increasing, because dense network structures were continuously generated after drying. In addition, UV-irradiated VT11-coated PLA film could retard the lipid oxidation more effective than PLA neat film and LDPE film. The film could be an alternative to maintain the quality and extend the shelf-life of shrimp crackers.

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Fan Wu

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LIST OF ABBRAVIATION

1. AIAA	Aluminum acetylacetone
2. AFM	Atomic force microscopy
3. BIE	Benzoin isobutyl ether
4. DCCAs	Drying control chemical additives
5. FTIR	Fourier-Transform Infrared Spectrometer
6. IPTES	Triethoxysilane
7. ICPTES	3-Isocyanatopro- pyltriethoxysilane
8. LDPE	Low density polyethylene
9. Nylon/ LLDPE	Nylon/ linear low-density polyethylene
10. N=C=O	Isocyanate group
11. -NH	Amine groups
12. PET	Polyethylene terephthalate
13. PV	Peroxide value
14. TBARS	Thiobarbituric acid reactive substances
15. OTR	Oxygen transmission rate
16. OPC	Oxygen permeation coefficient
17. -OH	Hydroxyl groups
18. PEG	Polyethylene glycol
19. PCL	Poly ε-caprolactone
20. PS	Polystyene
21. SEM	Scanning electron microscopy
22. TEOS	Tetraethyl orthosilicate
23. THF	Tetrahydrofuran
24. TMOS	Tetramethyl orthsilicate
25. TM7O1S	Trimethoxy (7-octen-1-yl) silane
26. VTES	Triethoxyvinylsilane
27. VT10	mole ratio VTES: TEOS=1: 0
28. VT14	mole ratio VTES: TEOS=1: 4
29. VT11	mole ratio VTES: TEOS=1: 1
30. VT41	mole ratio VTES: TEOS=4 :1

LIST OF ABBRAVIATION (Continued)

31. VT01	mole ratio VTES: TEOS=0: 1
32. WVTR	Water vapor transmission rate

CHAPTER 1

INTRODUCTION AND REVIEW OF LITERATURE

1.1 Introduction

Nowadays, human is facing a variety of environmental concerns, the pollution, greenhouse effect and fossil resource consumption. So, biodegradable materials have been attracting a great deal of interests, such as protein (Cinelli, *et al*., 2014), cellulose-fiber (Carlos *et al*., 2014), poly(lactic acid) (Raquez *et al*., 2013). Poly(lactic-acid), PLA, has an excellent biocompatibility, absorbability, non-toxic, and non-irritating. It can be completely decomposed into CO_2 and H_2O without pollution. PLA is currently one of the most attractive biodegradable polymers. Moreover, that of the process of PLA required 25-55% less energy than conventional petroleum materials. It makes PLA a lower cost in production (Rasal *et al*., 2010). In addition, the mechanical properties of PLA films were better than Polystyene (PS) and Polyethylene terephthalate (PET) (Jamshidian *et al*., 2010; Rasal *et al*., 2010). PLA is also widely used in biomedical polymer, textile and packaging industries now.

However, there are some disadvantages of neat PLA, such as low thermal resistance, excessive rigidity, slow crystallization rate, low heat distortion temperature, and higher cost as compared with other polymer resins. Moreover, PLA is limited to use as food packaging material, because PLA has low oxygen and water vapor barrier properties compared with conventional petroleum-based polymers (Bang and Kim, 2012). Thus, modification is playing a dominant role in the applications of PLA. The most common approach to solve this problem is to prepare organic- inorganic hybrid materials. Silica (SiO_2) has been proved to be one of the most popular candidates for preparing organic- inorganic coating materials to improve gas barrier properties, because there is a great natural abundance of silica in earth with low cost. Moreover, silica has high thermal resistance and good functionalizability surface (Raquez, 2013).

Sol-gel process is a simple method to produce good hybrid materials that it uses inorganic or metal alkoxide as a precursor and can homogeneously be mixed in the liquid phase. By ageing, slow polymerization between colloidal particles occurs, and three-dimensional network structure of the gel is formed. After drying, the molecule or nano-structure materials are obtained (Lenza *et al*., 2015).

This research aims to synthesize organic-inorganic hybrids by sol-gel method and use it as coating materials for PLA film. PLA will be used as an organic part and incorporated into the inorganic siloxane, which contains ethylene groups. Then the vinyl polymerization will be performed by UV-irradiating. Phase attraction of the hybrid will be increased, because the different inorganic phases (The polycondensed silane backbone) will be connected by covalent bond (self-assembled organic double bond). Based on the tortuous pathway concept, stronger phase attraction could enhance barrier properties by increasing the effective diffusion path length (Tokudome *et al.*, 2014).

Moreover, shelf life is a significant fact for food packaging. It is the duration for the food which retain good sensory, color, texture properties, physical, chemical and microbiological, and the food is stored under the recommended conditions. However, several factors affect the shelf life of the product, such as the lipid oxidation and moisture content in the environment (Muralidharan *et al.*, 2015). Therefore, it is important to analyze those factors and take required action to improve the keeping quality of food products.

Shrimp cracker is a popular food in most Asian countries. However, due to the porous structure, shrimp cracker is really sensitive to the environment. Thus, in this research, the shelf life of shrimp crackers was predicted by investigating the physical and chemical changes of shrimp crackers covered with coated-PLA materials, PLA neat film, LDPE film and nylon/LLDPE film during 56 days of storage at 30 ± 0.5 °C and 65 ± 5 % RH in comparison with the air fried shrimp cracker without packaging. In addition, moisture content, pH, color, crispiness and toughness of samples were investigated. The lipid oxidation of samples was also investigated by determining peroxide value (PV) and thiobarbituric acid reactive substances (TBARS).

1.2 Review of literature

1.2.1 Polylactic acid, PLA

1.2.1.1 Raw materials of lactic acid

Cheaper raw materials are very important for commercial products. Generally, lactic acid can be synthesized from cheap raw materials, such as corn, potato, rice and agro-industrial by-products. Additionally, these raw materials contain low level of contaminant and level toxic components. It is good for rapid production rate, because these raw materials capable of being fermented with little or no pre-treatment (Rojan *et al*., 2009). Table 1 presents raw material of lactic acid and its yield.

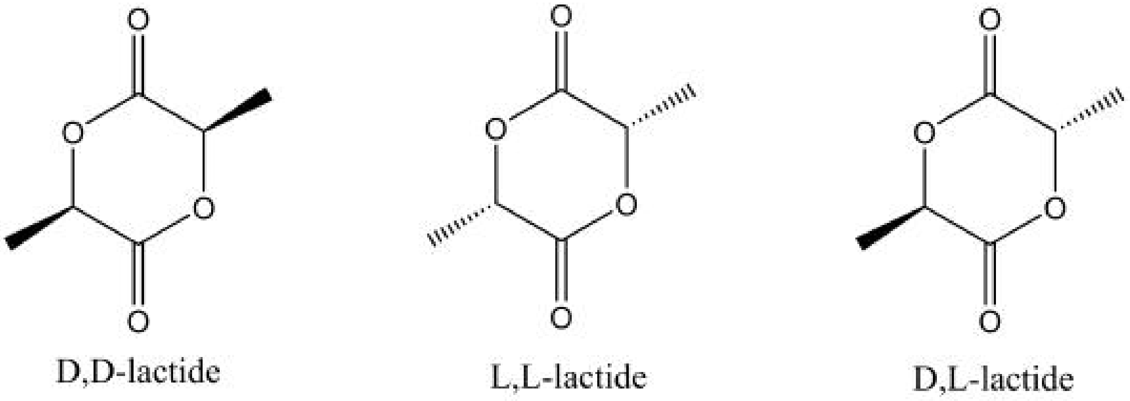
Table 1. Raw materials of lactic acid and yield

Raw material	Lactic acid yield
Wheat starch	0.77 to 1 g/g
Corn, rice, wheat starches	0.70 g/g
Potato starch	0.87 to 0.97 g/g
Wheat and rice bran	129 g/ l
Corn starch	0.935 g/g
Agro-industrial starchy waste	0.93 g/g
Cellulose	80 g/ l
Wood	0.85 g/g
Pre-treated wood	48–62 g/l
Waste paper	0.8 g/g
Wood hydrolysate	0.9 g/g

Source: Rojan *et al*., 2009

1.2.1.2 The structure of lactic acid

Lactide has two optical isomers due to two chiral centers: D-D lactide (D-LA) and L-L lactide (L-LA). But meso-LA (D, L-lactide) is also available, as well as rac-LA which racemic mixture D-LA and L-LA. The chemical structures of lactide are shown in Figure 1.



D,D-lactide L,L-lactide D,L-lactide

Figure 1 Chemical structure of lactide

Source: Raquez *et al*., 2013

1.2.1.3 Synthesis of PLA

Firstly, raw materials, such as corn, rice and potato are decomposed to glucose by enzyme-catalyzing. Then the glucose is transferred into lactic acid by continuous fermentation. Finally, PLA is synthesized by initiating polymerization. Generally, there are two methods to synthesize PLA; Direct condensation polymerization and ring-opening polymerization, shown in Figure 2 and Figure 3, respectively.

1.2.1.3.1 Direct condensation

Direct condensation of lactic acid monomers is not a frequent and common approach to synthesis PLA. This method leads to low molecular weight products, because the water causes chain-transfer reaction. The main advantages of direct condensation polymerization are no catalyst and simple process of polymerization, but the polymerization conditions are relatively harsh, such as high temperature at least 200°C and long reaction time. Furthermore, this sort of PLA products shows poor performance and no commercial application. So, this method does not have a good practical value (Kim *et al.*, 1999).

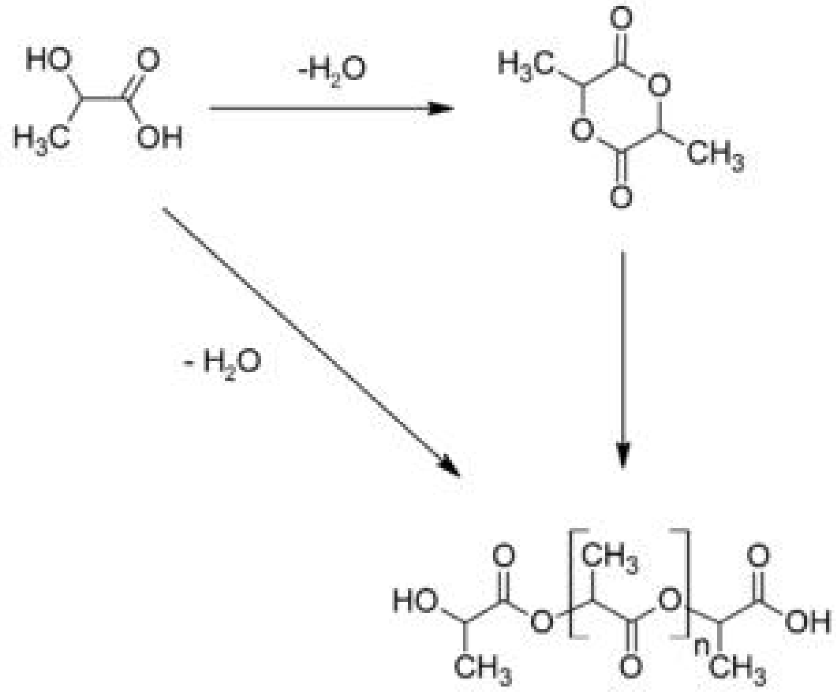


Figure 2 The process of direct condensation of lactic acid monomer

Source: Kim *et al.*, 1999

1.2.1.3.2 Ring-opening polymerization

Another route to produce PLA is ring-opening polymerization. This is also the most common route to produce PLA. High molecular weight PLA can be obtained by ring-opening polymerization of lactide with catalysts (generally is tin octoate ($Sn(Oct)_2$)) in the solution, the melt or the suspension. This kind of PLA resin presents excellent properties and commercial application (Garlotta, 2001).

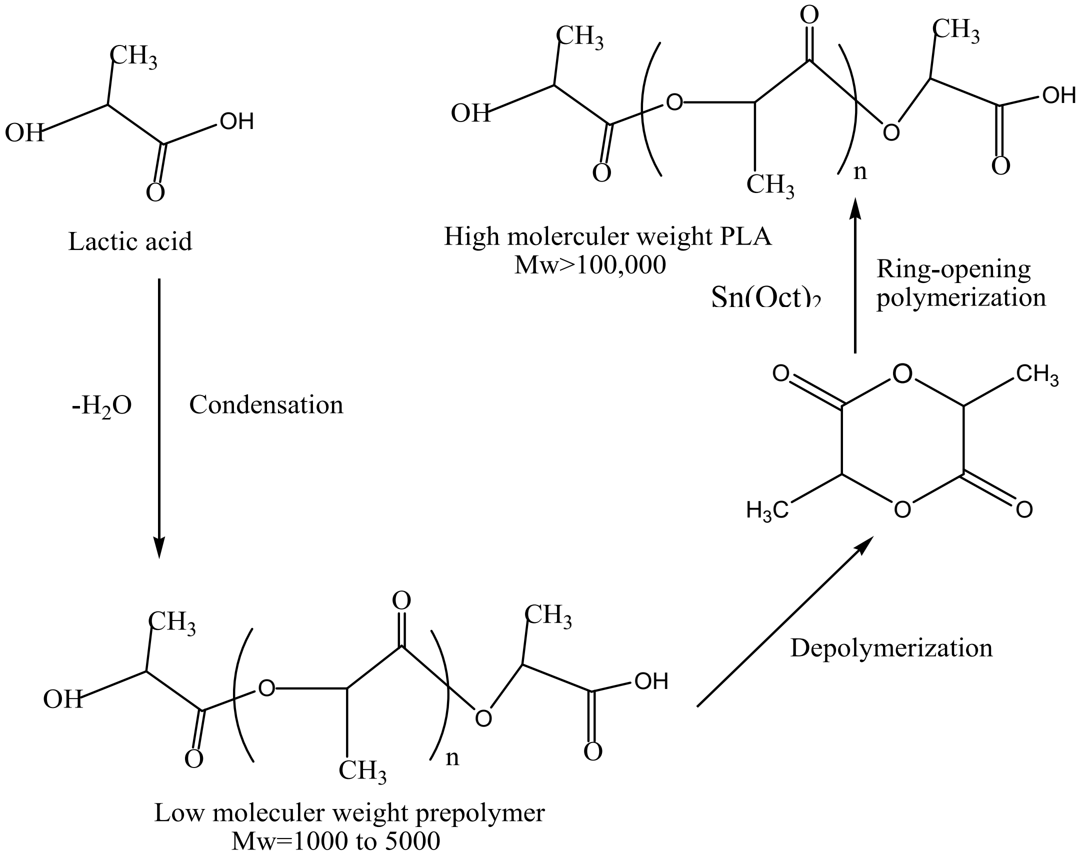


Figure 3 The process of ring-opening polymerization

Source: Garlotta, 2001

1.2.1.4 Properties of poly(lactic acid)

1.2.1.4.1 Physical properties

The crystallinity of PLA has the effect on melting point, heating resistance, mechanical properties, processing properties, as well as barrier properties. Drieskens *et al*., 2009 proved that the oxygen permeability of crystallized PLA was decreased by comparing with amorphous references.

However, the main factor which affected the crystallinity of PLA was the mixture ratio of L- lactic acid and D-lactic acid in materials (Saeidlou *et al*., 2012). The crystallinity can be increased with increasing the content of L-lactic acid. Neat PLA (poly-L-lactide or poly-D-lactide) is a semi-crystalline polymer (Södergård *et al*., 2002). When the crystallinity of poly-L-lactide was approximately 37%, a melting point was around 175-180°C, the glass transition temperature was about 60-65 °C and a tensile modulus was about 2.7-16GPa (Middelton *et al*., 2000).

1.2.1.4.2 Rheological properties

PLA resin can be made various useful products by thermal processing, such as extrusion and injection molding. Moreover, rheological properties of PLA are playing a dominant role in thermal processing. Crystallinity affected the rheological properties of PLA. In other words, different composition ratio of poly-L-lactide and poly-D-lactide had an effect on thermal processing. Higher crystallinity lead to higher shear viscosity. Fang, 1999 found that amorphous PLA had a lower shear viscosity than semicrystalline PLA. Then, PLA structure had an effect on rheological properties. Dorgan showed that the viscosity of linear structure was lower than branched structure in the Newtonian range, while viscosity of the linear structure was higher than branched structure in the non-Newtonian range (Dorgan *et al*., 2000).

1.2.1.4.3 Degradable properties

Generally, polymer degradable occurs due to main chain or side chain scission. However, there are various environmental factors affecting polymer degradation, such as hydrolysis, thermal activation, photolysis, biological activity, oxidation or radiolysis. This degradation also be referred to environmental degradation. PLA has better biodegradable properties than other conventional polymers. Its degradation is affected on a range of factors, such as crystallinity, purity, water vapor permeability, molecular weight and additives (Nampoothiri *et al*., 2010).

The degradable process of PLA is shown in Figure 4. Firstly, hydrolysis ester linkages (C-O bond) was embedded in the PLA backbone, and then it got further degradation occurred by enzyme catalysis. Finally, it was converted into carbon dioxide and water. Some people worried about the service life of PLA due to the good degradable property. Actually, PLA had a moderate degradable rate. Enzymolysis just started after hydrolysis. The degradable duration of PLA may be lasted from some weeks to 2-3 years. However, the degradable rate could be increased if buried it into ground with microbial and organic composite materials together.

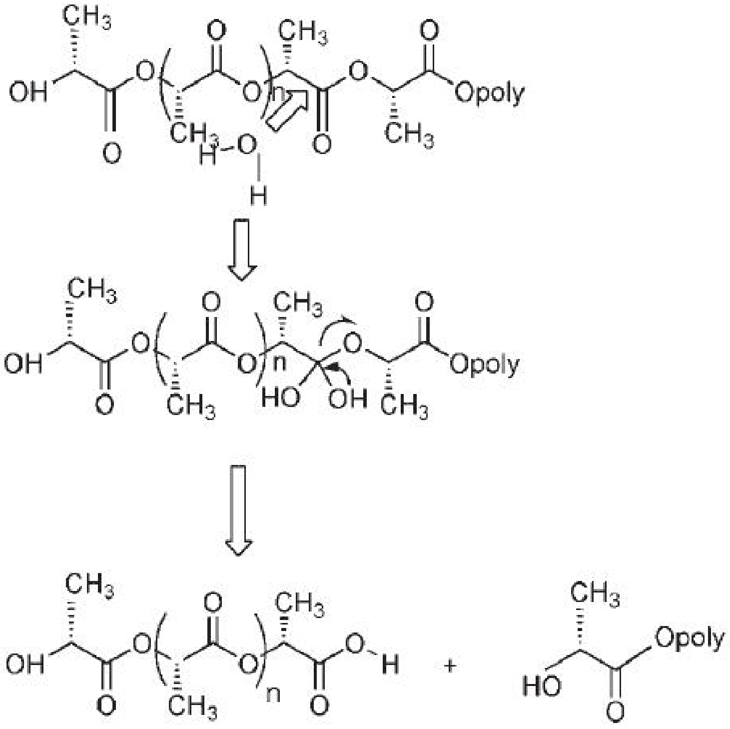


Figure 4 PLA hydrolysis and molecular weight loss

Source: Auras *et al.,* 2004

1.2.1.5 Applications of PLA

According to advantages mentioned earlier, PLA becomes one of the promising candidates for various industrial application fields, such as agriculture, pharmaceutical, medical, packaging and clothing (Auras *et al*., 2004). Especially, it pays a great deal of attention on medical field, because of its good biocompatible property and non-toxicity in the human body. Hamad indicated that PLA materials had a potential application in medical field, such as wound management, tissue engineering, drug delivery systems, as well as orthopedic devices (Figure 5) (Hamad *et al*., 2015).

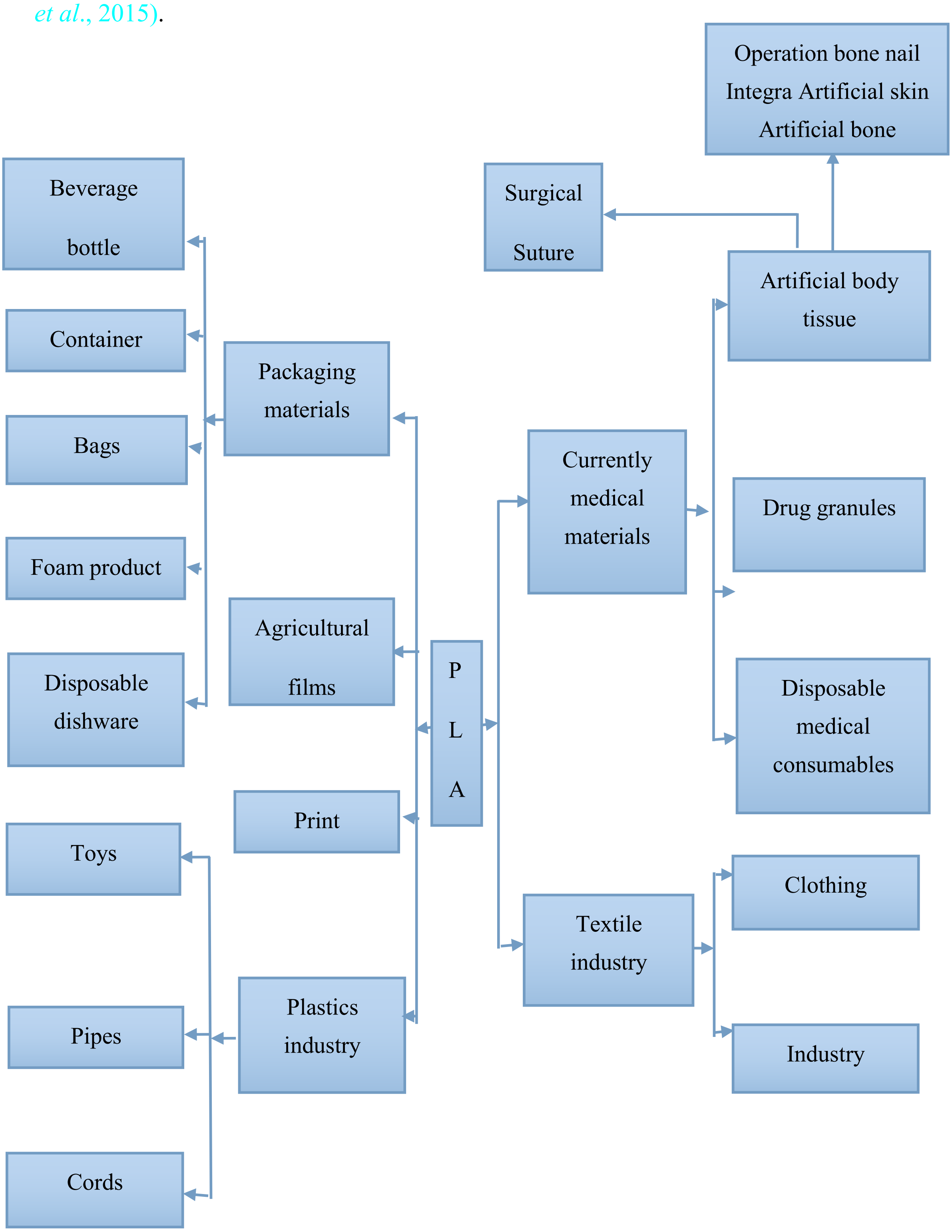


Figure 5 Application of PLA

Source: Auras *et al*., 2004; Hamad *et al*., 2015

Furthermore, in food packaging industry, the proper packaging materials are not only minimizing food loses, but also providing safety and extending shelf-life. Nanotechnology is generally used in food packaging field. It can improve performance of packaging materials, such as their water vapor barrier property, thermal property, chemical stability, heat resistance and biodegradability. Because PLA has good optical property and non-toxicity, it is highlighted to be used in food packaging fields. Rhim *et al*., 2013 found that PLA presented the potential application in the food packaging sector (Table 2).

Table 2. Applications of PLA in the food packaging field

Improved packaging properties
Enhanced biodegradation
Shelf life extension, oxygen scavenger, antimicrobial
Interaction with the environment, self-cleaning, self-healing, indication of deterioration
Nutraceuticals, bioactive compounds
Time temperature indicator (TTI), freshness indicator, leakage indicator, gas detector
Nanosensor: Indication of food quality, growth of microorganisms
Nanocoating
Antimicrobial

Source: Rhim *et al*., 2013

1.2.1.5.1 PLA processing technology

Generally, the possibilities methods of manufacture for PLA resin are extrusion, injection molding and blow molding (Żenkiewicz *et al*., 2010).

1.2.1.5.1.1 Drying

Drying is very important for PLA resin before next processing technologies. Because PLA resin is sensitive to humility content. The molecular of PLA face the risk of degradation at a high-relative humility during processing. It is necessary to dry the PLA resin with a moisture content less than 0.01%w/w for decreasing the risk (Jamshidian *et al*., 2010).

1.2.1.5.1.2 Extrusion

Extrusion is used as a common method to melt thermoplastic. It is also the first the step to make the PLA resin in films, containers, bags and so on.

1.2.1.5.1.3 Injection molding

Injection molding has a restriction to for PLA materials (Najafi *et al*., 2015). PLA is sensitive to humility content, which causes the molecular degradation during processing and it has an effect on the mechanical performance. Moreover, the injected molded PLA is relatively brittle, due to its intrinsic brittleness (Quiles-Carrillo *et al*., 2018).

1.2.1.5.1.4 Blow molding

Generally, extrusion blow molding, injection stretch blow molding, and injection blow molding are wide used. The extrusion blow molding process can make the films of PLA different thicknesses. (Lim *et al*., 2008). The injection blow molding is normally to produce small bottles, and it is less to use for PLA processing. Because the method requires low degree of melt strength and the equipment is expansive. The injection stretch blow molding is used to produce the PLA bottles for food packaging, especially it is a good container for fresh fruit juices and sport drinks (Jamshidian *et al*., 2010).

1.2.1.5.2 PLA film

Generally, PLA film can be prepared by casting film extrusion, injection blow molding and solvent casting. Bang and kim, 2012 used a single screw extruder to prepare the PLA film by casting extrusion process. Di Miao et al., 2014 using casting extrusion process to produce PLA neat film and PLA active film in a small-scale cast film pilot plant. In addition, Scaffaro et al., 2017 successfully prepared the PLA monolayer film by film blowing process in two different extruders equipped. Moreover, Gao et al., 2017 and Byun et al., 2015 prepared PLA films by solvent casting method. PLA resin was dissolved in methylene chloride and stirred. And then PLA solution was distributed into dishes or glass plates. The methylene chloride was evaporated at 25°C for 24 h to ensure no solvent residual in the films, and then the film was stored at 4°C until time of use.

For the research on PLA's properties. Auras *et al*., 2004 indicated that PLA films had higher barrier properties for ultraviolet light than low density polyethylene (LDPE) but slightly lower than those of poly(ethylene terephthalate) (PET), polystyrene (PS) cellophane. (See in Figure 6). Table 3 shows the mechanical of two PLA films by the names of 4030-D, 4040-D which was made with nominally 98% L-lactide, and 94% L-lactide resins, respectively, in comparison with PET films and PS films. PLA films had higher values of tensile strength than PS but lower than PET. And PLA film has a similar elastic modulus values with PS and PET. Jamshidian *et al*., 2010 indicated that the physical properties of PLA film could be promoted by orientation. It was also found in PET film and PS film. Furthermore, PLA had good thermal properties and it was good for heat sealing. Auras *et al*., 2004 proved that both 4030-D and 4040-D PLA film had lower glass transition temperature and melting temperature than PET and PS. However, Auras *et al*., 2005 indicated that

PLA film had a higher water vapor transmission rate (WVTR) than PET and PS, and PLA film had a relatively higher oxygen transmission rate (OTR) than PET and a relatively lower than PS.

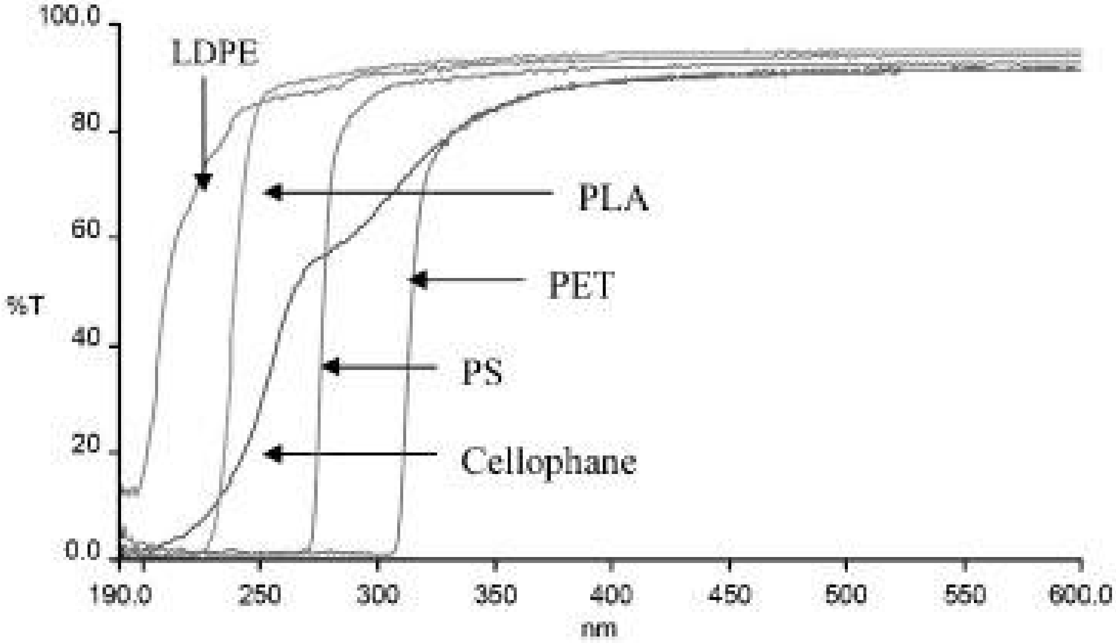


Figure 6 Percent transmission versus wavelength for PLA(98%L-lactide), PS, LDPE, PET and cellophane films.

Source: Auras *et al*., 2004

Table 3. Mechanical properties of poly(98% L-lactide), poly(94% L-lactide), PS and PET films.

	Poly(98% L-lactide)		Poly(94% L-lactide)		PS Biaxial	PET
	MD	CD	MD	CD		
Tensile yield stress MPa (kpsi)	72 (10.5)	65 (9.5)	84 (12.2)	74 (10.7)	55-82 (8-12)	275 (40)
Percent elongation at yield	5	4	3	4	-	~6
Percent elongation at break	11	5	78	97	3-40	60-165

Table 3 (Continued)

	Poly(98% L-lactide)		Poly(94% L-lactide)		PS Biaxial	PET
	MD	CD	MD	CD		
Elastic modulus GPa (kpsi)	2.11 (306.4)	2.54 (368.3)	2.31 (335.4)	2.87 (416.3)	3.2 (464)	2.8-4.1 (400-600)

Source: Auras *et al*., 2004

Table 4. Oxygen and water vapor transmission rate of PLA, PET and PS at 22 °C. The thickness of PLA and PET is 18, 20 and 18 mm, respectively.

Properties determined	Units	PLA	PET	PS
WVTR	[g/ (m^2/day)]	15.30± 0.04	3.48± 0.02	5.18 ± 0.03
OTR	[cc/(m^2/day)]	56.33± 0.12	9.44± 0.06	531.58 ± 0.67

Source: Auras *et al*., 2005

Moreover, PLA is a good packaging material for markets. In particular, PLA film have received an increase attention in packaging application. Siracusa et al., 2012 studied whether PLA film was a good packaging material by preparing and investigating four PLA films, which were PLA with SiO_x coating, PLA with anti-UV coating and PLA varnished in comparison with natural PLA film. The author indicated that PLA films, which combined with a synthetic polymer, could provide a good application in packaging fields. This PLA materials were best in current market solution. On the other hand, the author further indicated that PLA film should be researched in real life environmental conditions.

1.2.1.6 Modification of PLA

1.2.1.6.1 Bulk modification

Bulk modification of polymers represents a technologically attractive and a relatively simple method. Modification is achieved during the forming process, and no need of an additional modification step. The major limitations of PLA are its slow degradation rate and bad ductility. Rasal *et al*., 2010 indicated that many bulk modification methods can promote degradation behavior, crystallinity, mechanical properties (mainly toughness), and processability of PLA.

1.2.1.6.2 Co-polymerization

The controlled degradation of PLA was interfered due to its high crystallinity. It also decreased the compatibility with soft issue and not be good for the application of PLA as a biodegradable material. So, it is a very significant goal of researchers to provide controlled degradation profiles for PLA-based polymers. Ouchi *et al*., 2004 succeeded synthesizing different lactic acid co-polymers, such as random and block co-polymers of PLA. They found that PLA-grafted polysaccharide had a potential application for biodegradable medical materials. Co-ploymerization method can decrease the regularity and crystallinity of molecular chains by the incorporation of another chain into PLA backbone. Generally, it can strengthen the hydrophobicity, crystallinity and hydrophilicity of materials by adjusting the ratio of lactic acid or other monomers. The materials which were co-polymerized with PLA and presented good performance were polyethylene glycol(PEG) (Toncheva *et al*., 2016) and poly ε-caprolactone (PCL) (Cohn *et al*., 2005). The polyesters which can be co-polymerized with PLA are shown in Figure 7.

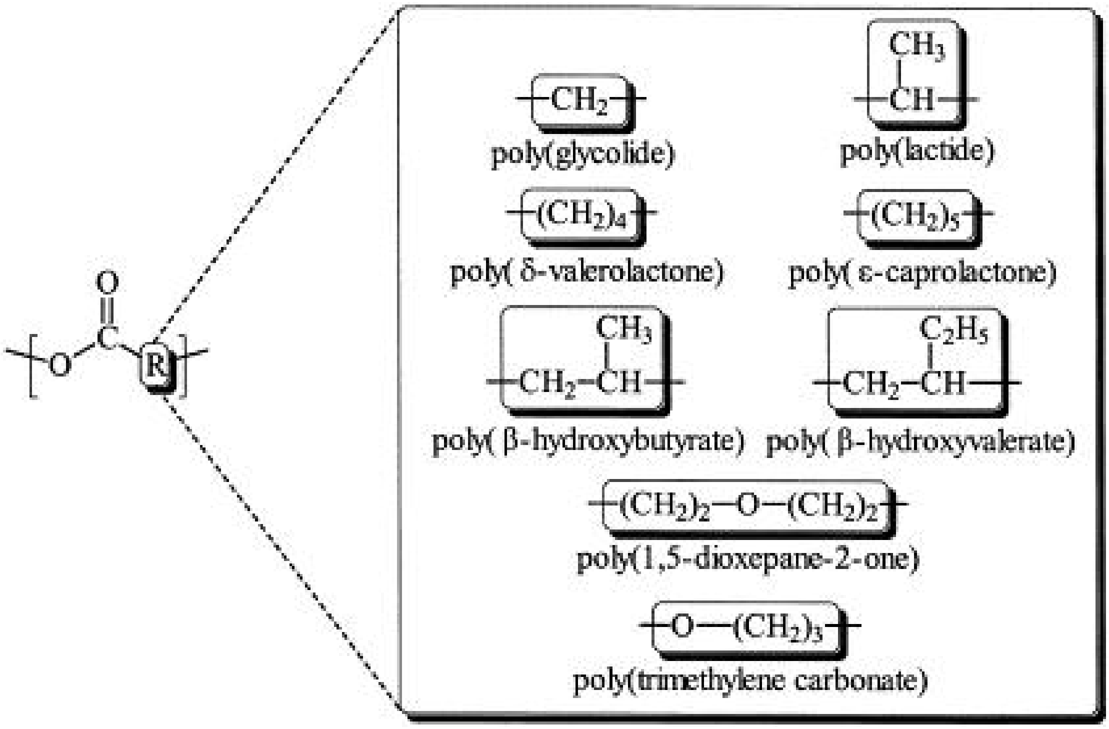


Figure 7 Repeating units of the most common lactic acid-based co-polymers

Source: Södergård *et al*., 2002

1.2.1.6.3 Blending

Blending technology which needs at least two polymers are blended to form a new material with better mechanical properties. It not only retains the original excellent performance, but also shows new behavior due to the synergistic effect among different components. Hillmyer and co-workers found that the toughness was improved by blending PLA with low density polyethylene (LDPE) (Wang and Hillmyer, 2001; Anderson *et al*., 2003). Patrício and Bártolo, 2013 prepared PCL/PLA blends. The rheological measurements were indicated that these blends had a good thermal stability, especially good for the extrusion process.

1.2.1.6.4 Surface modification of PLA

Surface modification is the act of modifying the surface of materials and maintaining the original properties by bringing physical, chemical or biological characteristics. This method can be classified by permanent and non-permanent surface modification (Rasal *et al*., 2010). It is required to control the topography, functionalities, roughness and hydrophilicity. Jordá-Vilaplana found that the wettability of PLA was improved by promoting the surface energy of an atmospheric plasma surface treatment. This method was easy to establish and it did not generate wastes, as well as it was the continuous industrial production (Jordá-Vilaplana *et al*., 2014).

1.2.2 Sol-gel method

1.2.2.1 Introduction of sol-gel method

The earliest reports of sol-gel method could be traced back to the middle of the nineteenth Century. Kistler prepared the silica aerogel by sol-gel method as the first practical application in the early 1930s. For a brief period at the end of 1960’s and early 1980’s, sol-gel technology showed a clear progression by the effort of a large number of scientists (Sakka, 2013).

Sol-gel process is a simple method to produce good hybrid materials that it uses inorganic or metal alkoxide as a precursor, and then all chemicals are homogeneously mixed in the liquid phase. By ageing process, slow polymerization between colloidal particles occurs, and three-dimensional and network structure of the gel is formed. After drying, the molecule or nano-structure level materials are obtained. Hydrolysis and polycondensation of sol-gel process are shown in Figure 8. An example of the hydrolysis and condensation process of Tetraethyl orthosilicate (TEOS), which is a typical kind of alkoxysilane molecule, can be seen in Figure 9.

Hydrolysis : $\equiv Si{-}OR + H_2O \rightarrow \equiv SiOH + ROH$ (1)

First step

$$Si(OR)_4 + H_2O \rightarrow Si(OR)_3(OH) + ROH \qquad (2)$$

Second step

$$Si(OR)_3(OH) + H_2O \rightarrow Si(OR)_2(OH)_2 + ROH \qquad (3)$$

Third step

$$Si(OR)_2(OH)_2 + H_2O \rightarrow Si(OR)(OH)_3 + ROH \qquad (4)$$

Fourth step

$$Si(OR)(OH)_3 + H_2O \rightarrow Si(OH)_4 + ROH \qquad (5)$$

Condensation $\equiv Si(OH) + ROSi\equiv$

$$\rightarrow \equiv Si{-}O{-}Si\equiv + ROH \qquad (6)$$

Condensation $\equiv Si(OH) + (HO)Si\equiv$

$$\rightarrow \equiv Si{-}O{-}Si\equiv + H_2O \qquad (7)$$

Figure 8 Hydrolysis and polycondensation of sol-gel process

Source: Sakka, 2013

The hydrolysis process of $Si(OH)_4$-ROH-H_2O-catalyst system is presented in step (1) (Figure 8). The hydrolysis process of an alkoxysilane molecule is shown in step (2) to step (5), then the condensation process is taken place as shown in step (6) and step (7). There are various products involved with this reaction. All above reaction equations are simple expressions of the hydrolysis and condensation. The true reactions are more complicated (Sakka, 2013).

Tetraethyl orthosilicate (TEOS) is a well-studied alkoxide. It is an important chemical precursor for sol-gel processing, because it easily reacts with water to build a huge silicon-containing molecule (or macromolecule) and form a dense network structure.

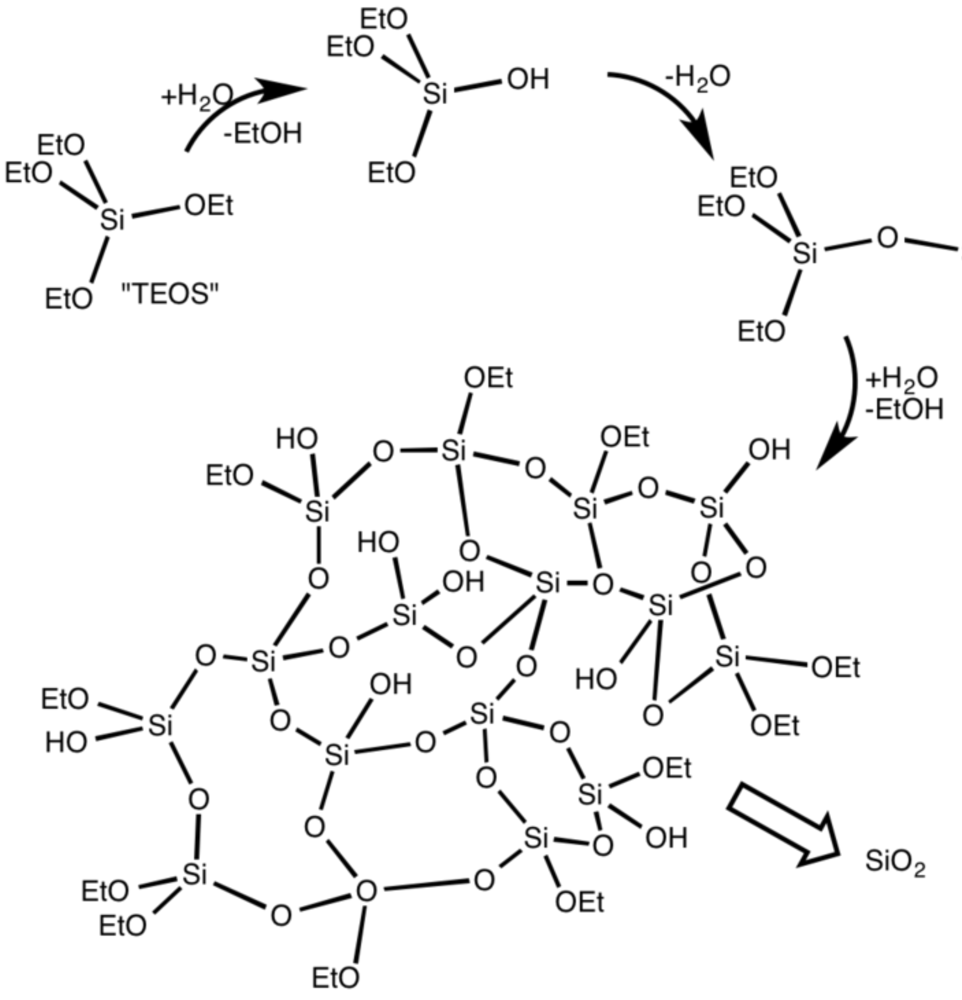


Figure 9 The hydrolysis and condensation process of TEOS in sol-gel method

Source: https://en.wikipedia.org/wiki/Sol-gel#/media/File:SolGelCartoon.png

There are three kinds of microstructures on the surface of gel by sol-gel processing, including porous, dense and organic-inorganic microstructures, which are shown in Table 5. The organic-inorganic and porous microstructures are presented at low or around room temperature.

Table 5. Microstructures on the surface of gel

Microstructures		Examples of Materials
Porous		Silica aerogels Silica columns for liquid chromatograph
Dense	Glasses	Silica glass preforms for optical fiber
	Polycrystalline materials	Ferroelectric coating films Titanium oxide coating
	Inorganic-organic hybrid	Silica glass with dispersed metal and semiconductor colloids
Organic- inorganic	Distributed organic and inorganic species bonded with each other	Polymethylmethacrylate-silica- titania
	Inorganic or hybrid matrix with dispersed organic molecules and pigments	Silica film with dispersed molecules

Source: Sakka, 2013

One of the significant advantages of Sol-gel processing is the low-temperature processing. Organic-inorganic hybrid materials can homogeneously mix at nanostructure level. Sol-gel technology is a commercial method. It also covers a large range of functional products, such as photonic, electronic, optical, thermal, mechanical, chemical, biochemical, as well as biomedical materials. Some of significant sol-gel-derived materials with different functions are shown in Table 6-8.

Table 6. Sol-gel-derived materials with photonic and electronic functions

Function	Specific function or microstructure	Examples
Photonic	Generation of light	Lasers; Phosphors
	Transmission of light	Optical fiber preforms; Planar optical waveguide.
	Optical absorption	Colored automobile window
	Electrochromism	WO_3 Electrochromic film
	Sensing	H_2S sensor
	Antireflection	Antireflective coating films
	Photovoltaic effect	Graezel type solar cell
	Photocatalysis	Photocatalyst

Table 6 (Continued)

Function	Specific function or microstructure	Examples
	Transparent conductor	Transparent electrode of In_2O_3
Electronic	Ferroelectric	Ferroelectric materials (Capactitors, non-volatile memories).

Source: Sakka, 2013

Table 7. Sol-gel-derived thermal and mechanical materials

Function	Specific function or microstructure	Examples
Thermal	Heat resistance	Silica- alumina- boria fibers
	Thermal insulation	Aerogel
Mechanical	Mechanical protection	Hard coat on plastic lens
	Nanopatterning	Nanopatterned film
	Spacer	SiO_2 spherical particles for LCD panel spacer.

Source: Sakka, 2013

Table 8. Sol-gel-derived materials with chemical, biochemical and biomedical Functions

Function	Specific function or microstructure	Examples
Chemical	Catalysts	CeO_2- ZrO_2 catalyst for oxidation
	Membrane	Asymmetric membrane for filtering
	Macropores	Porous silica monolith for HPLC
	Water repellent	Fluoroalkysilane hybrid coating for automobile window
	Passivation	Organic- inorganic hybrid coating
	Barrier properties	Organic- inorganic hybrid
Biochemical and biomedical	Artificial tissue	Encapsulation of pancreatic cells and artificial bone.
	Diagnosis	Antibodies in gel for immunoassay
	Lab on a chip device	DNA arrays

Source: Sakka, 2013

1.2.2.2 Drying and thermal process

The condensation reaction of sol-gel process cannot stop after hydrolysis reaction. The moisture and solvent will be removed by drying. There are three different phenomena can be seen when the moisture and solvent are removed by drying: persistent shrinkage, hardening and stress rupture. No capillary force in the wet gel during the drying process, because the gel pores are filled with liquid phase. At the beginning, the volume of lose gel is equal with evaporated part. With further evaporation, the particles are gathered together under a capillary pressure when the volume of lose gel is lower than evaporated part. Gel cracking by stress due to the size of capillary pores is different in the gel, then it generates different capillary pressure. An approach which can overcome this drawback is the incorporation of drying control chemical additives (DCCAs) into the starting mixture solution before gelation (Lenza *et al*., 2015).

1.2.2.3 The dominant advantages of sol-gel process

- Good interfacial adhesion between organic-inorganic phase is provided by producing thin bond-coating.
- Good corrosion protection performance is provided by producing thick coating.
- Materials can be shaped into complex geometries in a gel state.
- High purity products can be produced.
- Reaction occurs at low temperature.
- Fine powers can be created.
- The coating can be provided by an effective, simple and economic method.
- It has good cost effectiveness.

Carter and Norton, 2013 indicated that sol-gel method was easy to control the purity and composition of products. The products could also be deposited films and coated on a wide variety of surfaces. Compared to other vapor-phase methods, sol-gel method enabled better flexibility. Carter and Norton pointed out that the equipment of small-scale sol-gel processing in the laboratory was simple and inexpensive, such as three-necked flask, mechanical stirrer and constant temperature bath.

1.2.3 Related research

The earliest commercial application of sol-gel processing was thin films and coating. This technology was simple and applicable to a range of substrates, such as tubes, pipes and fibers. Hussain *et al*., 2018 indicated that sol-gel process could tailor the adhesion between the coating materials and different substrates, due to it provide thin mesoporous coatings high structural homogeneity.

Currently, sol-gel processing is a good method to produce gas and water vapor barrier coating films, because it can form three-dimensional network and dense structure materials. Bang *et al*., 2012 used PLA and Tetraethoxysilane (TEOS) as organic polymer and inorganic silicate precursor, respectively, to prepare biodegradable hybrid nanocomposites. Triethoxysilane (IPTES), a silane coupling agent, was used to increase the interfacial attraction between the PLA and silica. This material had good optical transmittance, and water vapor and oxygen barrier property improvement.

However, how to improve the phase attraction between organic and inorganic phases is a crucial aspect, because strong attraction can suppress the phase separation in the hybrid material. Shimojim and Kuroda, 2000 found that the double bonds (-C=C-) which were embedded in hybrid structure promoted vinyl polymerization by UV irradiation under the inert gas atmosphere for 12h. Shimojima *et al*., 2007 further researched the structure-property relations of hybrid materials. It was indicated that the same phenomena of polymerization occurred by UV-irradiating (Figure 10). Moreover, these hybrid materials presented an increase of hardness, because of adjacent siloxane layers were connected with strong covalent bond by vinly polymerization. The hybrid materials also showed a stronger resistance to an alkaline solution.

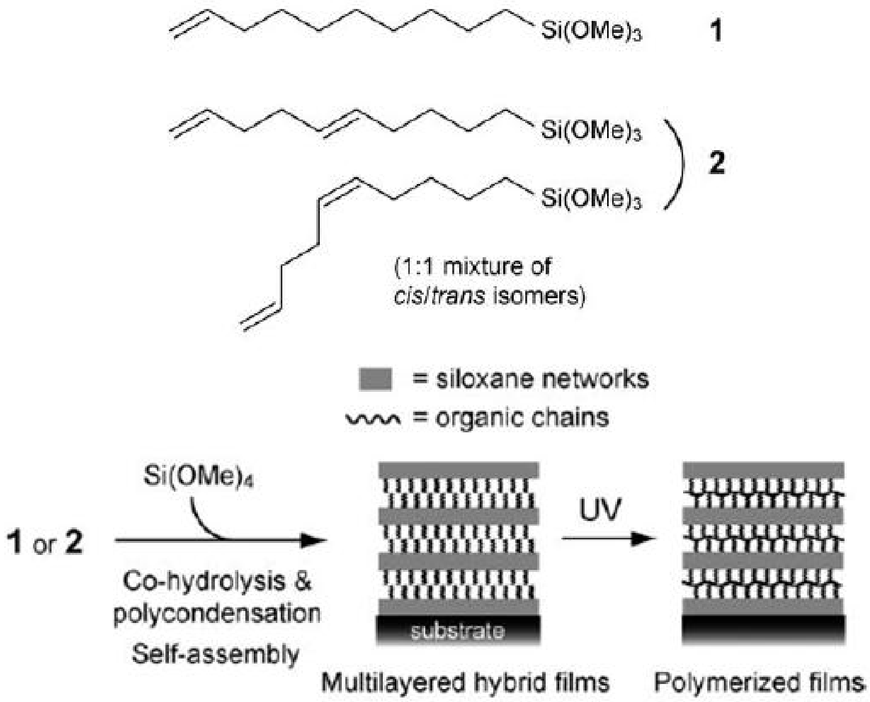
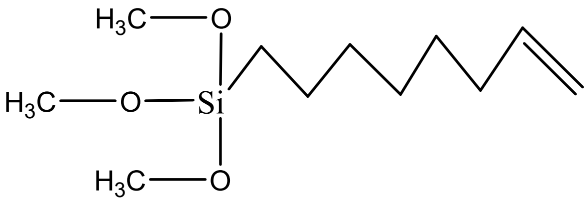


Figure 10 Formation processes of multilayered hybrid films

Source: Shimojima *et al*., 2007

Tokudome *et al.,* 2014 mixed tetramethyl orthsilicate (TMOS) with unsaturated organotrimethoxysilane, trimethoxy (7-octen-1-yl) silane (TM7O1S), and used as precursors. Their structures are shown in Figure 11. After sol-gel reaction, the gel was coated on Cu substrate, then the vinyl polymerization was initiated by using the UV light to irradiate the film for 12h in the inert gas atmosphere. This material showed a transparency of 98%, high thermal properties, good water vapor barrier property, and a scratch hardness of 6H-pencil.

1. TM7O1S



2. TMOS

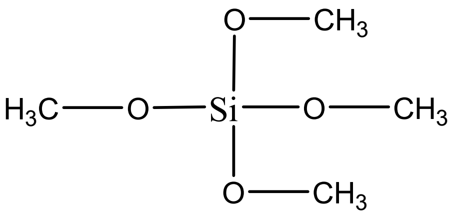


Figure 11 The chemical structure of TM7O1S and TMOS

Nevertheless, TM7O1S is expensive. It has not widely been used. Triethoxyvinylsilane (VTES) which has similar structure to TM7O1S, but it is cheaper than TM7O1S by market survey. Shin *et al.,* 2008 indicated that VTES was self-hydrolyzed, then after nuclei formation and growth, the vinyl groups were spread on organic-silica surface that could be performed the polymerization (Figure 12). This silica particles modified with polymers showed higher weight loss than unmodified silica particles because of the decomposition of the organic polymers grafted onto the particles. The surface modification of silica particles with polymers decreased the zeta potential values of the silica surface. Modified silica particles had lower water vapor adsorption due to the hydrophobic surface property resulting from the polymers grafted onto the silica surface. Isnin *et al.,* 2008 used VTES as a precursor, and benzoin isobutyl ether (BIE) and aluminum acetylacetone (AIAA) were used as a photoinitiator and a polymerization catalyst, respectively. This hybrid material was coated on a glass substrate. Next, the vinyl polymerization was performed by using UV-irradiation. Figure 13 shows FTIR spectra of VTES films. It proved that a change of C=C bonds to C-C bonds, the vinyl polymerization was occurred. The sharp peak around 1600 cm^{-1} was assigned to C=C stretching bonds. After UV irradiation, the intensity of that band decreased to about 50 %. This can be explained by a reduction of vinyl C=C bonds to C-C bonds due to the UV irradiation process. Polymerization occurs in the VTES film when the propagation reaction of free radicals from the photoinitiator with the precursor's vinyl bonds depletes C=C bonds and produce C-C bonds to form the organic network.

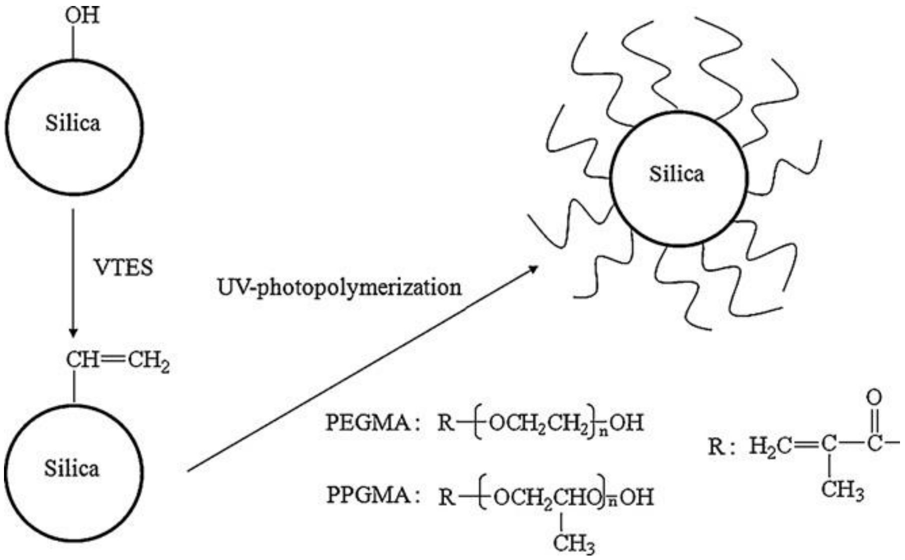


Figure 12 Polymer was grafted onto silica nanoparticles by UV-polymerization

Source: Shin *et al*., 2008

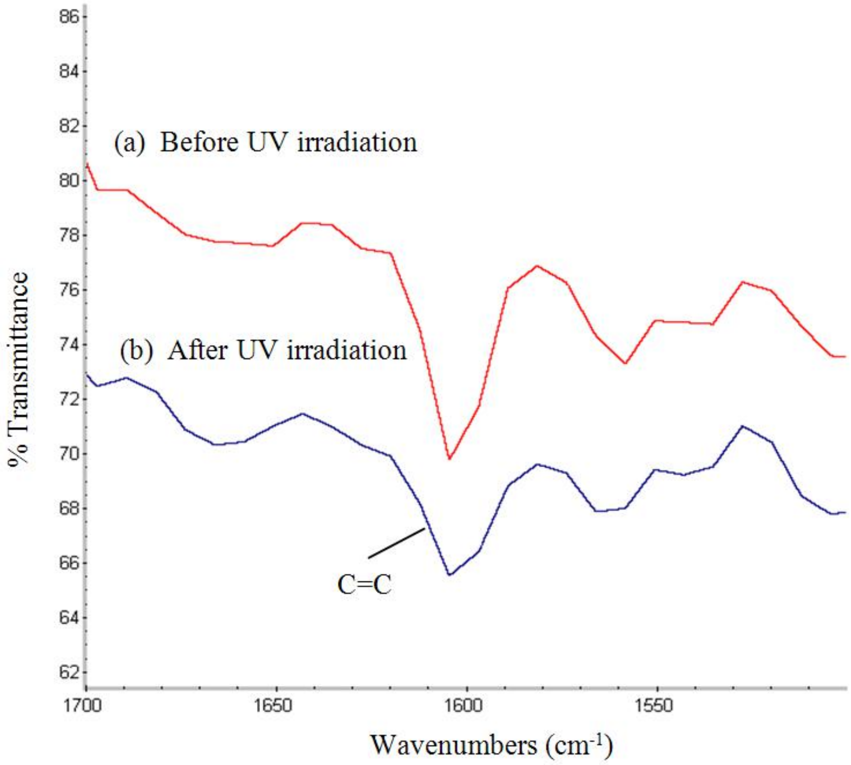


Figure 13 FTIR spectra of VTES films. (a) no UV irradiation and (b) UV irradiation for 10 min

Source: Isnin *et al*., 2008

TEOS was easily to be hydrolyzed to oxidize silicon in the water, it could form dense and cross-linking structure after condensation polymerization (Sakka, 2013). Phase attraction between two the organic and inorganic had a significant effect on the production high performance hybrid film, because the microphase separation could be suppressed by strong phase attraction in the materials (Bang *et al*., 2012). Therefore, VTES could be used as a coupling agent to treat silica nanoparticles and introduce reactive groups (C=C bonding), and perform vinly polymerization via UV-irradiation (Shin, 2008). 3-Isocyanatopro- pyltriethoxysilane (ICPTES) also could be used as silane coupling agent (Figure 14). Moreover, the hydroxyl groups in PLA (–OH) could connect with isocyanate (N=C=O) groups in

ICPTES and formed into the urethane group (Bang *et al*., 2012). Thus, ICPTES could promote phase adhesion.

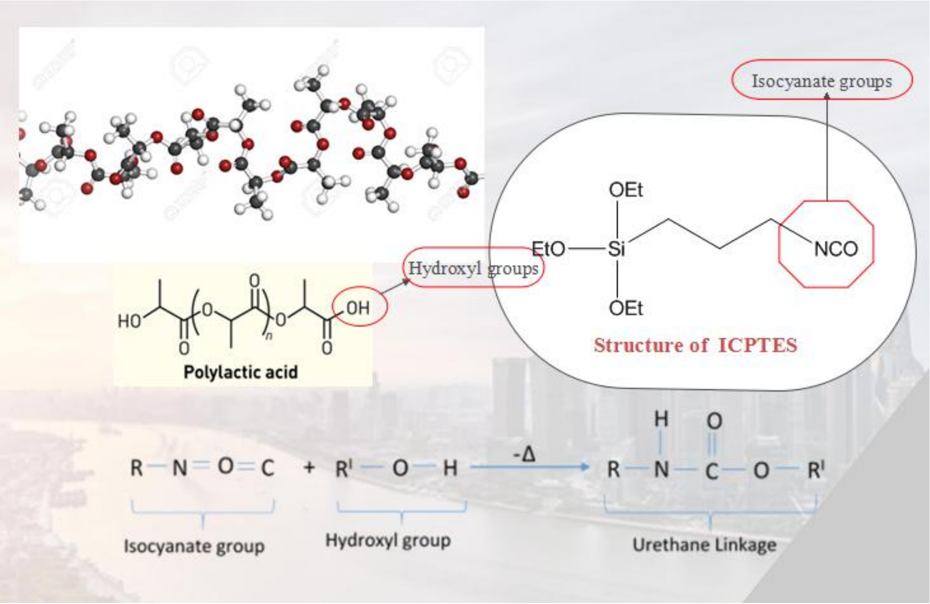


Figure 14 Reaction of hydroxyl group and isocyanate group

Source: Bang *et al*., 2012

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1.3 Objectives

1.3.1 To synthesize PLA/siloxane hybrids by sol-gel method and characterize their structure and properties.

1.3.2 To investigate the effect of the mole ratio of tetraethylorthosilicate(TEOS)/ vinyltriethoxysilane (VTES) on the barrier property.

1.3.3 To investigate the oxygen and water vapor barrier properties of coated-PLA film in comparison with LDPE film, nylon/ LLDPE film and PLA neat film.

1.3.4 To investigate the quality change of shrimp crackers packaged in coated-PLA film.

CHAPTER 2

SYNTHESIS AND CHARACTERIZATION OF SILICA HYBRID COATING MATERIALS FOR POLY(LACTIC ACID) FILM

2.1 Abstract

New silica/ poly(lactic acid) hybrid materials were synthesized by sol-gel method and used as coating materials to promote the oxygen and water vapor barrier property of PLA films. The mixtures of Tetraethoxysilane (TEOS) and Triethoxyvinylsilane (VTES), containing a reactive double bond were used as the inorganic silicate precursors to construct the siloxane network structure by co-hydrolysis and polycondensation reaction. Polymerization of the unsaturated bonds occurred by UV irradiation, as evidenced by sharp decrease of FTIR band at 1600 cm^{-1}, corresponding to terminal C=C stretching bond. Moreover, the phase attraction between the coating hybrid and the substrate was a crucial factor to increase the performance of the materials. In this study, PLA and 3-Isocyanatopropyltriethoxysilane (ICPTES) were used as an organic polymer and a silane coupling agent, respectively. FTIR absorption band at 1550 cm^{-1} was specified to the formation of amine groups (-NH), due to isocyanate groups in ICPTES reacting with hydroxyl groups in PLA chains. SEM was indicated that there were big cracks on the surface of coating materials without ICPTES. The water vapor barrier property of coated film showed a great improvement by 24.6% at the VTES/ TEOS ratio of 1: 1 (VT11), and the oxygen permeation coefficient (OPC) of VT11-coated film was decreased 24.8%, as compared to PLA neat film. In addition, the water contact angle of VT11-coated film decreased by 6.6%. XRD showed that the crystallinity of VT11-coated film was decreased after UV-irradiation for 1h. UV-irradiated VT11-coated film had a small water contact angle and AFM further presented it have a rather smooth surface. Moreover, the water vapor barrier property was improved with the aging time

increasing, because dense network structures were continuously generated after drying.

2.2 Introduction

Current human society faces a variety of environmental concerns, such as pollution, greenhouse gas effect and fossil resource consumption. Biodegradable materials, such as polyhydroxybutyrate (Arrieta et al., 2016) and poly(lactic acid) (Raquez *et al*., 2013) have long been the interest of research to solve the environmental issues. Poly (lactic-acid), or PLA, is a non-toxic and non-irritating material with excellent biocompatibility and absorbability. It can be completely decomposed into CO_2 and H_2O without causing pollution. PLA is thus currently one of the most attractive biodegradable polymers. In addition, the mechanical properties of commercially available PLA films are better than polystyene (PS) and PET spell out (Jamshidian *et al*., 2010; Rasal *et al*., 2010). Currently, PLA is widely used as biomedical polymer, and in textile and packaging industries.

However, PLA is limited in the application as a food packaging material. This is because PLA has low oxygen and water vapor barrier properties compared with conventional petroleum-based materials (Bang and Kim, 2012). One of the common approaches to solve this problem is to prepare organic-inorganic hybrid coating materials. Silica (SiO_2) has been proved to be one of the most popular candidates for preparing organic- inorganic coating materials to improve gas barrier properties, because there is a great natural abundance of silica on earth with low cost. Moreover, silica has high thermal resistance and good functionality surface (Raquez *et al*., 2013).

Sol-gel process is a simple method to produce good hybrid materials. The process uses inorganic or metal alkoxide as a precursor and can be homogeneously mixed in the liquid phase. By aging, slow polymerization between colloidal particles occurs, and a three-dimensional network structure of the gel is formed. After drying, the molecules or nano-structure materials are obtained (Lenza *et al*., 2015).

In this study, we reported a novel strategy to synthesize organic-inorganic hybrids by sol-gel method and its application as coating materials for PLA film. PLA was used as an organic part and incorporated into the inorganic siloxane, which contains ethylene groups. Then vinyl polymerization was performed by UV-irradiation. Phase attraction of the hybrid was increased, because the different inorganic phases (the polycondensed silane backbone) were connected via covalent bonds (self-assembled organic double bonds). Based on the tortuous pathway concept, stronger phase attraction could enhance the water vapor and oxygen barrier property by increasing the effective diffusion length.

2.3 Materials

2.3.1 Chemicals

The chemicals and materials and their purposes are shown in Table 9 and Table 10, and the main chemical structure, molecular weight (MW) and density are shown in Table 11.

Table 9. Experimental chemicals and their purposes

Chemicals	**Purposes**
Tetraethyl orthosilicate (TEOS, Aldrich, USA, 99%)	Inorganic silica precursor

Table 9 (Continued)

Chemicals	**Purposes**
Triethoxyvinylsilane (VTES, Shanghai Aladdin Biochemical Technology Co., Ltd., 97%)	Inorganic silica precursor, and coupling agent to strengthen phase attraction
3-Isocyanatopropyltriethoxysilane (ICPTES, Shanghai Aladdin Biochemical Technology Co., Ltd., 95%)	Coupling agent to strengthen phase attraction
Benzoin Isobutyl Ether (BIE, Zhejiang Maya-Reagent Co., Ltd., 95%)	Photoinitiator
Polylactic acid resin (PLA 2002D, NatureWorks LLC)	The organic polymer in the PLA/Siloxane hybrid materials
Tetrahydrofuran (THF, RCI labscan, 99.8%)	Co-solvent to increase the reaction rate of hydrolysis during sol-gel process when VTES, TEOS and water were mixed
Hydrocholoric acid (Hcl, Loba chemie 35.4%)	Analyst, to promote hydrolyze reaction rate

Table 10. Experimental materials and their purpose

Materials	**Purposes**
PLA film (35μm)	Coating substrate, control
LDPE film (32μm)	Reference
Nylon/ LLDPE film (75μm)	Reference

Table 11. The structure, molecular weight and density of main chemicals

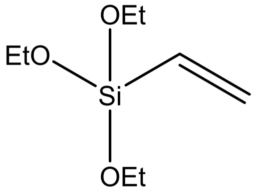
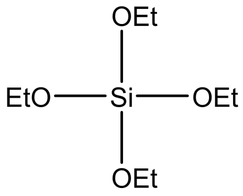
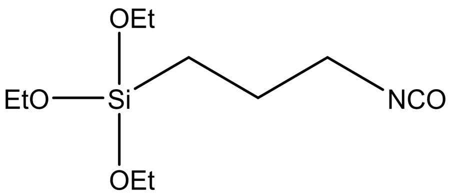
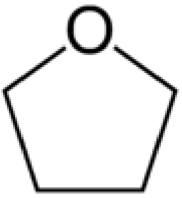
Chemicals	**Structure**	**Molecular weight**	**Density**
Triethoxyvinyl silane (VTES)		190.31	0.9100
Tetraethyl orthosilicate (TEOS)		208.33	0.9300
3-Isocyanatopropyltriethoxyslane (ICPTES)		247.36	1.000

Table 11 (Continued)

Chemicals	**Structure**	**Molecular weight**	**Density**
Tetrahydrofuran (THF)		72.11	0.888

2.4 Equipments

The equipment used in this experiment are shown in Table 12.

Table 12. List of equipment used in the research

Instrument	**Model**	**Company/ Country**
Fourier-Transform Infrared Spectrometer (FTIR)	EQUINOX 55	Bruker, Germany
Scanning electron microscopy (SEM)	Quanta 400	FEI, Netherland
Water contact angle	COCA 15 ED	Dataphysics, Germany
X-ray diffraction	X’ Pert MPD	Philips, Netherlands
Ultraviolet–visible spectroscopy	UV-1601	Shimadzu, Japan
Atomic force microscopy (AFM)	easyScan 2	Nanosurfn AG, Switzer- land

Table 12 (Continued)

Instrument	Model	Company/ Country
Bar coater	F99000	Feldham 2, Austriag
Magnetic stirrer	RO 10 power	Kikal labortechnik, Germany
Micrometer	ID-C112PM	Kawasaki-shi, Japan

2.5 Methodology

The experimental procedure and reaction are shown in Figure 15 and 16, respectively.

2.5.1 Preparation of PLA/ Siloxane hybrid coating materials

PLA/ Siloxane hybrid coating materials were prepared by sol-gel method (Bang and Kim, 2012). Firstly, a mixture of (VTES and TEOS)/ H_2O/ THF at mole ratio of 1: 2: 6 was stirred for 3 h to partially hydrolyze the VTES and TEOS under acid analyst at room temperature. Hydrochloric acid was used as catalyst to improve the reaction rate, as well as the pH of solution was adjusted to 2, the rate of hydrolysis reaction was promoted in acidic situation (Sakka, 2013). The composition of the solution was VTES: TEOS at mole ratio of 1:4, 1:0, 1:1, 0:1 and 4:1, respectively (Tokudome *et al*., 2014). The total amount of TEOS and VTES was 0.03 mol. Secondly, 1 g PLA resin was dissolved in THF solvent to prepared 5 wt% PLA solutions with homogeneous dispersion. Moreover, PLA resin was modified by adding 0.001mol silane coupling agent, ICPTES and stirred for 3 h at 60°C (Bang and Kim, 2012). The partially hydrolyze inorganic siloxane precursor and total modified

PLA solution were mixed and stirred for 3 h at room temperature (The detail amount of each chemicals was shown in Table 13). Finally, 0.001mol benzoin isobutyl ether (BIE) was added to the solution with the VTES/ BIE molar ratio of 5/ 100 as a photoinitiator. The solution was further stirred for an hour.

Table 13. The detailed amounts of reactants

VTES: TEOS	(VTES+TEOS) / mol	VTES/ mol	TEOS/ mol	H_2O/ mol	THF/ mol	Total/ mol
VT10	0.03	0.030	0	0.06	0.18	0.27
VT14	0.03	0.006	0.024	0.06	0.18	0.27
VT11	0.03	0.015	0.015	0.06	0.18	0.27
VT41	0.03	0.024	0.006	0.06	0.18	0.27
VT01	0.03	0	0.03	0.06	0.18	0.27

2.5.2 Vinyl polymerization

The resulting gel of VT01, VT14, VT11, VT41 and VT01 was aged and put in a closed packaging which contained silica gel for 12h. Then the samples were irradiated under UV light at 30000lux for 1 hour. Moreover, the control sample was also prepared without UV irradiation.

2.5.3 Coating process

The UV-irradiated gel was coated on the PLA film by using a bar coater. PLA film was supported from Thai Polymer Association, was with thickness of 35μm. The PLA film was cut to the same area as A4 paper and the surface was cleaned with ethanol. Next, the film was spread on the coating machine. 2ml gel solution was used for coating each film at the coating speed of 90mm/s. Finally, all the coated films were dried in a drying oven at 60°C for 24h. The middle part of film would used for characterization.

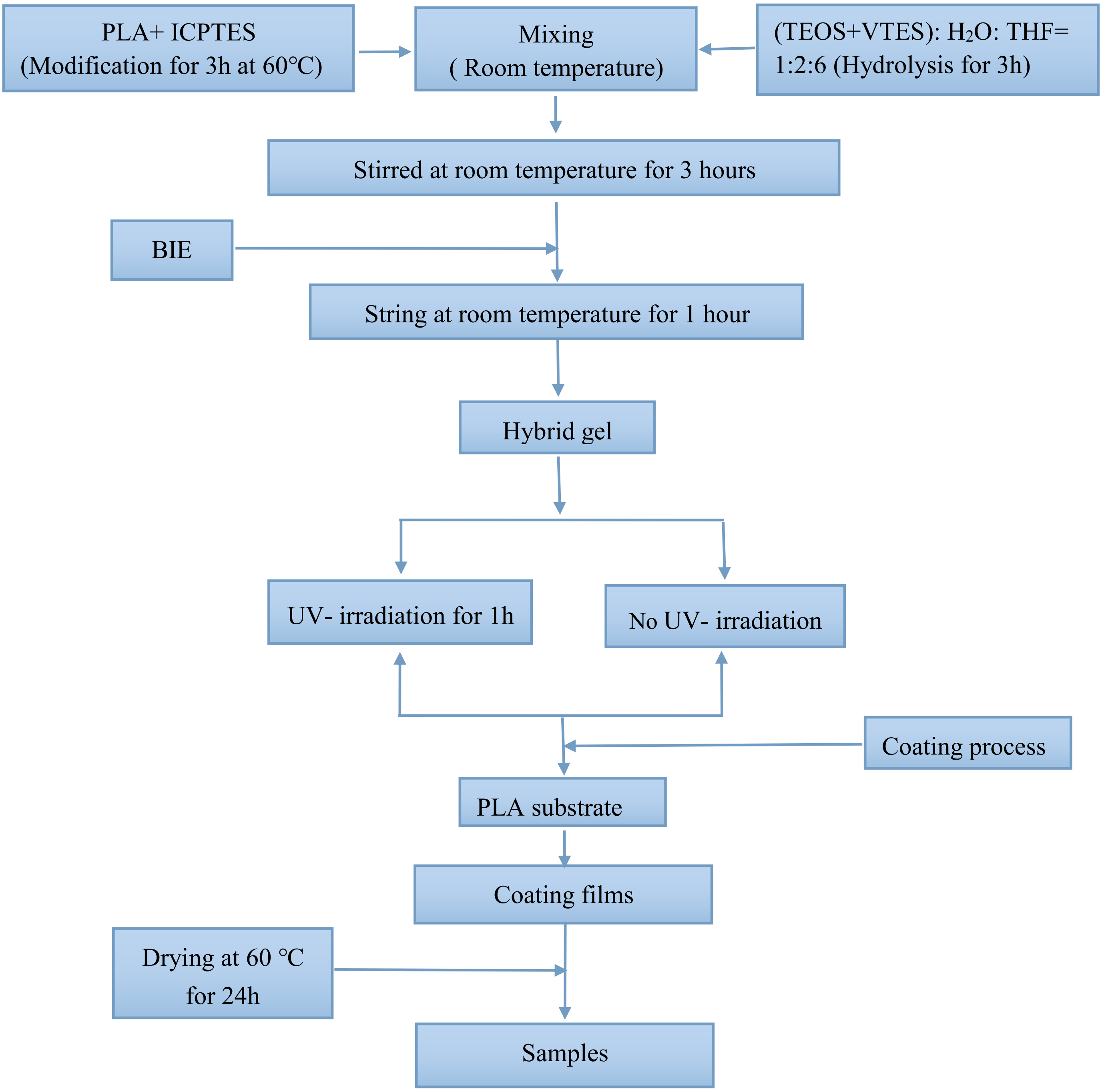


Figure 15 Experimental procedure

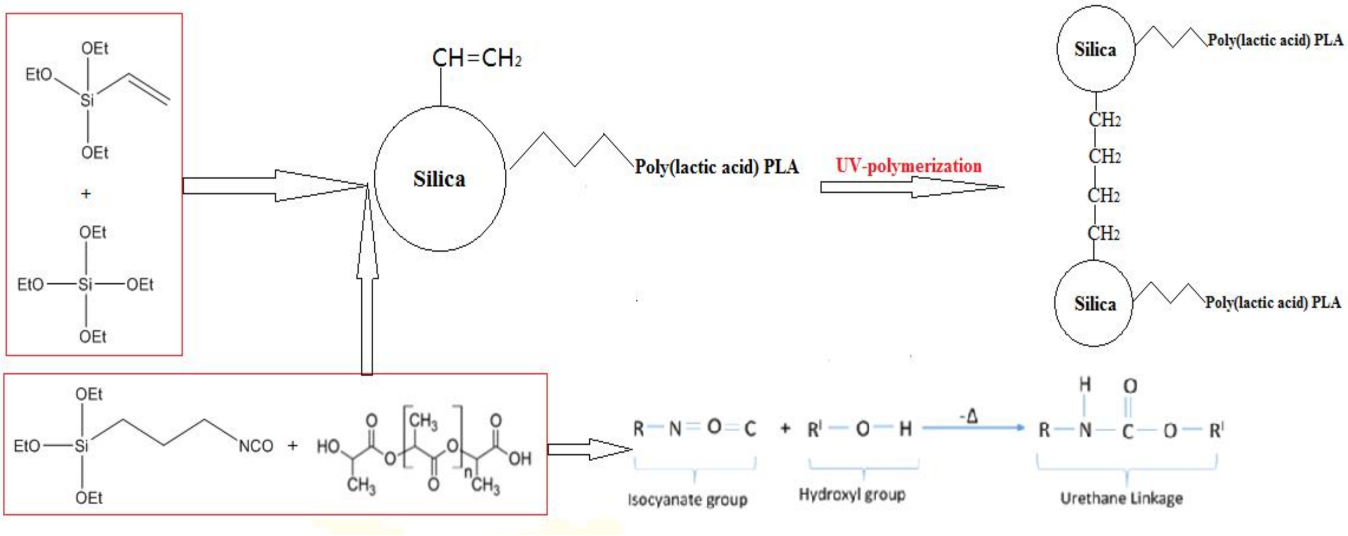


Figure 16 Experimental reaction

2.6 Characterization

2.6.1 Scanning electron microscopy (SEM)

Coating materials were fractured under liquid nitrogen. Then, the samples were mounted on bronze stub and sputtered with gold to make the sample conductive. The photographs were taken at an acceleration voltage of 15 kV.

The thickness of coating gel was measured by SEM.

2.6.2 Fourier transform infrared spectroscopy (FTIR)

Coating materials were diluted with KBr power and pressed them into pellets less than 1mm thick. The spectra was collected in the range of 400–4000 cm^{-1} at a resolution of 4 cm^{-1} and scan number of 32.

2.6.3 X-ray diffraction (XRD)

The crystallinities of hybrid films were characterized by X-ray diffraction and operated at 40 kV and 30 mA. Measurement was performed in the range of 1-30° at a scanning rate of 1.0°/min.

2.6.4 Film thickness

The thickness of film was measured by using micrometer.

2.6.5 Atomic force microscopy (AFM)

The morphology of coating materials, was also observed by 2D and 3D AFM analysis. Area roughness parameters for any M × N rectangular image were calculated as follows:

$$\mathrm{S}_a = \frac{1}{N}\sum_{1-0}^{N-1}\left|Z(x_1)\right|$$

$$\mathrm{R}_\mathrm{q} = \sqrt{\frac{1}{N}\sum_{1-0}^{N-1}\left(Z(x_1)\right)^2}$$

Where S_a is the average roughness, while R_q is the root-mean-squared roughness.

2.6.6 Water vapor permeability (WVP)

WVP was investigated by using ASTM, 1989. LDPE and nylon/ LLDPE films were used as references. Briefly, the hybrid coated PLA films and the reference films were cut to the diameter of 7.5 cm circles and their thickness were measured. Each sample was put on the permeability cups (Alumina cups) which contain enough dried silica gel (0% RH) and measuring their weight. Finally, all samples were placed in environmental chamber at 25 °C and 50% RH, and the weight of each sample should be recorded every day until one week. WVP-value was calculated by using the following equation:

$$\mathrm{WVP}\ (\mathrm{gm^{-1}s^{-1}Pa^{-1}}) = \mathrm{wlA^{-1}t^{-1}(P_2 - P_1)^{-1}}$$

Where w is the weight gain of the cup (g); l is the film thickness (m); A is the exposed area of film (m^2); t is the time of increase (s); P_2 - P_1 is the vapor pressure difference across the film (Pa).

2.6.7 Oxygen transmission rate (OTR)

OTR was measured by using an oxygen transmission rate tester according to ASTM standard D3985. LDPE and nylon/ LLDPE films were used as references. The test temperature was set to 23°C and the RH was set to 0% relative humidity. The test area of coated PLA films and the reference film were considered 50 cm^2. While measuring the sample, the film was separated into two chambers in a permeation cell, pure oxygen was passed on the upper side of the sample film, and pure nitrogen was passed on the lower side of the sample film. Oxygen was permeated into nitrogen part through the film. OTR values were obtained from the instrument.

2.6.8 Water contact angle

The wettability of the coated-PLA film, PLA neat film, LDPE film and nylon/ LLDPE film was performed by a contact angle meter at ambient temperature. 1 µl of distilled water was dropped onto the surface of a sample and the contact angle was recorded by a CCD camera. All images of the droplets on the surface of the specimens were analyzed by Image J software (Jongnavakit *et al*., 2012).

2.7. Experimental result and discussion

2.7.1 Fourier-Transform Infrared Spectroscopy (FTIR)

For organic–inorganic hybrid materials, the phase attraction had a crucial effect on the production of high performance hybrid film, because the micro-phase separation could be suppressed by strong phase attraction in the material. 3-Isocyanatopropyltriehoxysilane (ICPTES) was used as silane coupling agent here, because the urethane groups could be formed between hydroxyl groups (–OH) in PLA and isocyanate (N=C=O) groups in ICPTES (Bang and Kim, 2012).

As shown in Figure 17, the strong band at 1750cm^{-1} was related to the carbonyl bond (-C=O) in PLA chains. The broad and strong band at 1200cm^{-1} to 1000cm^{-1} was due to the siloxane framework (Si-O-Si) stretching modes. The peak band at around 1550cm^{-1} was ascribed to amine group (-NH). The result indicated that the strong covalent bonding was successfully formed between hydroxyl groups in the PLA chains and isocyanate groups in ICPTES.

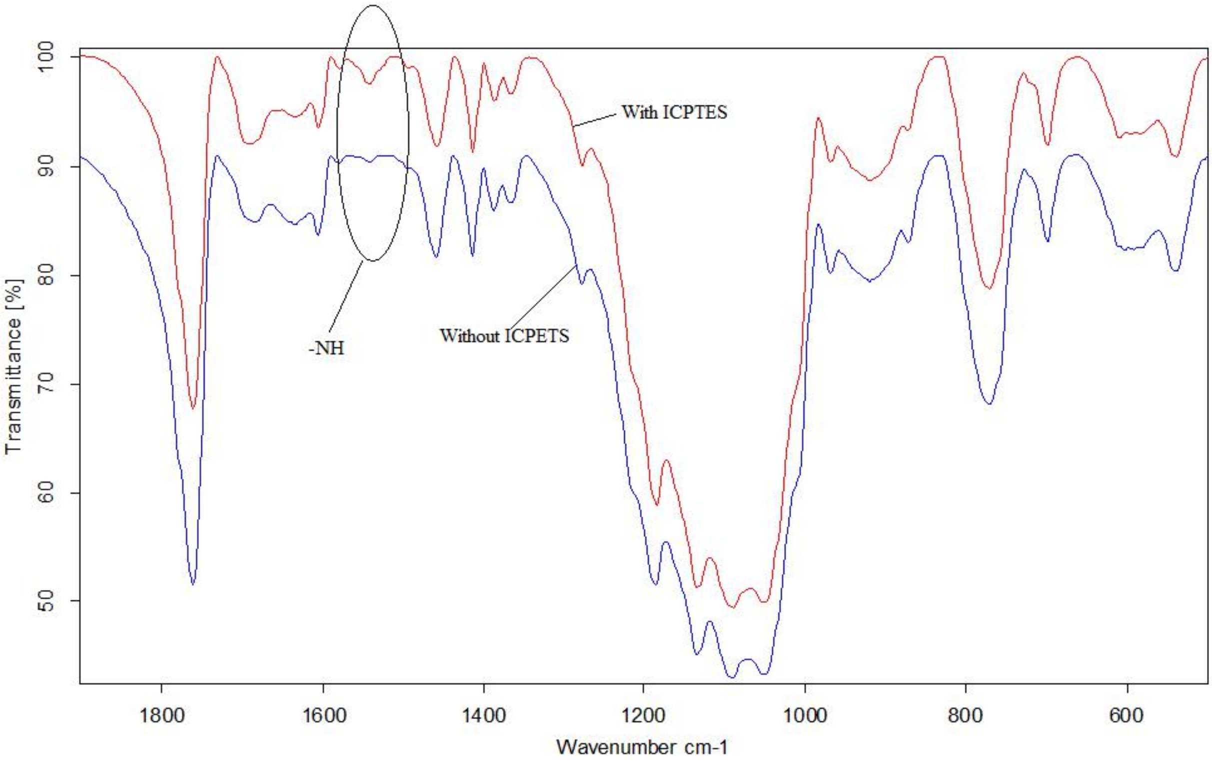


Figure 17 Comparison of FT-IR spectra for the coated-PLA without ICPTES and that with ICPTES

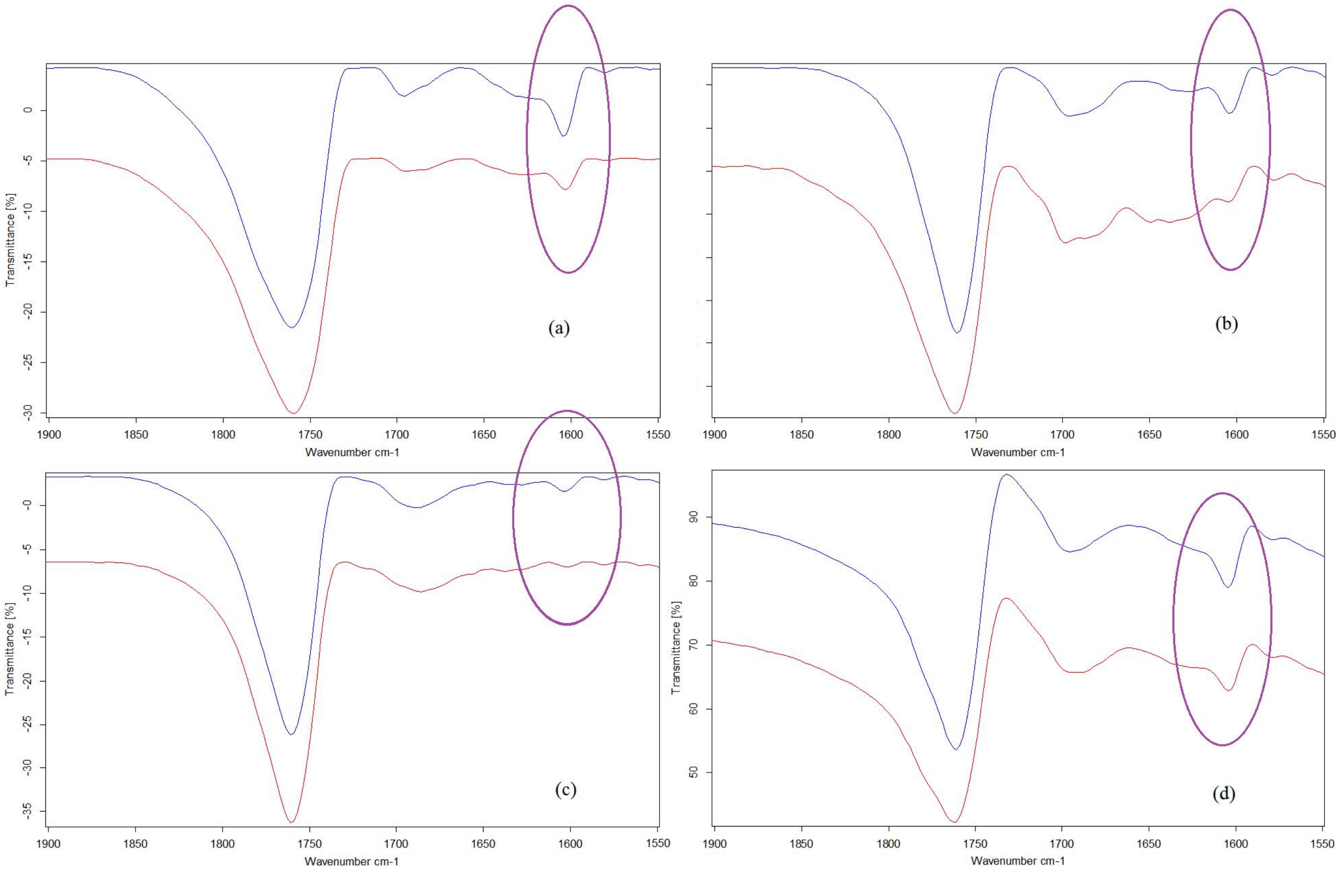


Figure 18 Comparison of FT-IR spectra of the coated-PLA before and after UV irradiation. (a). VT10 (b). VT11 (c). VT14 (d). VT41. (Red line: After UV-irradiated 1h. Blue line: No UV-irradiation)

Not only a precursor, VTES could also be used as a coupling agent to treat silica nanoparticles and introduce reactive groups (C=C bonding). Polymerization of VTES occurred and formed the organic network when the free radicals from the photoinitiator (BIE) and the vinyl bonds from VTES were performed the propagation reaction to depletes C=C bonds and produce C-C. Figure 18 shows the comparison of FTIR spectra of coated-PLA materials before and after UV irradiation. The band at 1600 cm^{-1} was corresponding to terminal C=C stretching bond, and it presented a sharp decrease to 50% after UV irradiation in all samples. This indicated that the vinyl polymerization occurred between C=C bond. It also indicated that the C=C bonds could not be totally transferred to C-C bonds after

UV-irradiation for 1h for all composition ratios of VTES and TEOS. This result suggested that the radical reaction was not performed in the whole molecular chains of VTES. On the other hand, the peak band of C-O bond at around 1630 cm^{-1} did not change with UV-irradiation. This could also be used as a benchmark for comparison.

2.7.2 Water vapor permeability (WVP)

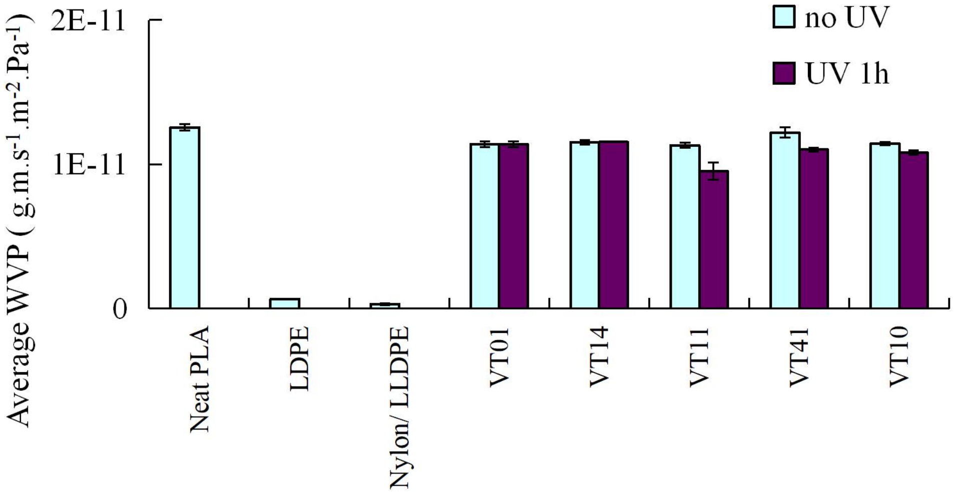


Figure 19 WVP with different composition of VTES/ TEOS ratio and before and after UV-irradiation in comparison with PLA neat film, LDPE film and nylon/ LLDPE film.

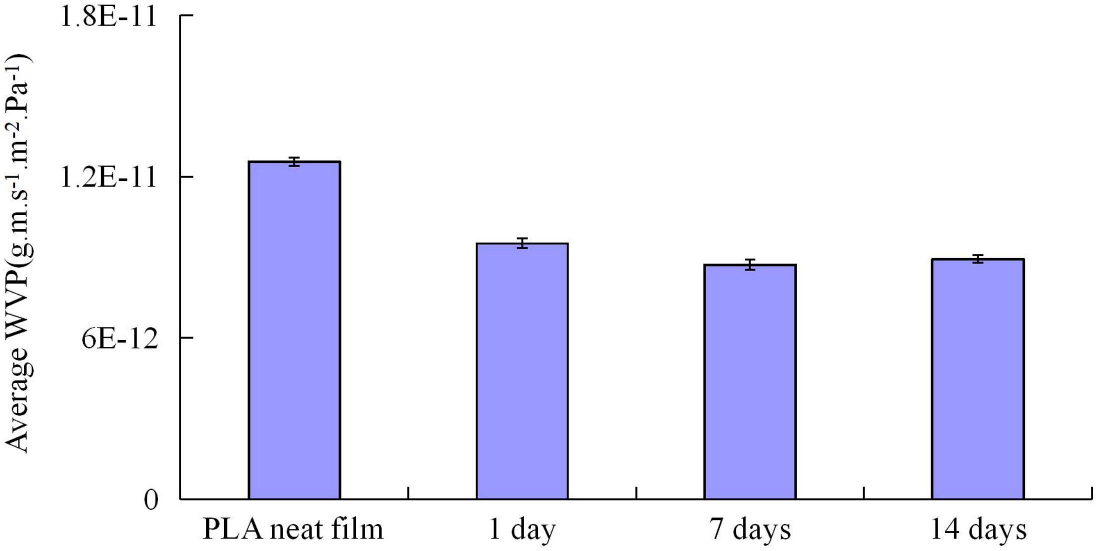


Figure 20 WVP of UV-irradiated VT11-coated film during different aging days

WVP of coated films for VT01, VT14, VT11, VT41 and VT10 and before and after UV- irradiation in comparison with PLA neat film, LDPE film and nylon/ LLDPE film was depicted in Figure 19, respectively. A decreased of WVP values for VT11, VT41 and VT10 coated-PLA film was observed after UV irradiation for 1h, due to the phase attraction and the stability of microstructure was improved by converting C=C bonding into C-C bonding and connected together (Isnin *et al*., 2008). It provided a higher effective water vapor diffusion length and increased the barrier properties (Tokudome *et al*., 2014). Moreover, it found that WVP values did not change significantly before and after UV-irradiation for VT01 and VT14 coated-PLA film, because of very low mount of VTES, indicating a small number of C=C bonds.

Furthermore, WVP values of UV-irradiated coated films for VT10, VT41, VT11, VT14 and VT01 were decreased at 16.4%, 12.7%, 24.6%, 8.1% and 9.3%, respectively, compared with PLA neat film. It indicated that the amount of mole ratio of VTES and TEOS had a crucial effect on barrier properties of coated-PLA films. On the one hand. VTES could be performed the vinyl polymerization to increase the phase attraction and decreased the WVP values of coated films. On the other hand. The high amount of TEOS could provide dense silica network structure. Because TEOS had four alkoxyl groups, which alkoxyl can be hydrolyzed and formed condensation reaction (Brinker and Scherer, 2013), and it resulted in a homogeneous dispersion of nano-silica particles in the continuous matrix and WVP was decreased.

However, UV-irradiated coated film for VT10 had a more significant decrease of WVP values than VT01. It proved that VTES was more effectively to increase the water vapor barrier properties of coated film than TEOS (Lee *et al*., 1999). Nevertheless, a great decrease of WVP by 24.6% for UV-irradiated VT11 coated film. It demonstrated that UV-irradiated VT11-coated materials presented the best water vapor barrier properties, because of the high dense network structure and high phase attraction were formed. Moreover, nylon/ LLDPE film and LDPE film had lower WVP values than coated-PLA film. Thus, the further improvement of water vapor barrier properties for coated-PLA film was still needed.

Figure 20 shows the WVP of the UV-irradiated VT11-coated film during 1, 7 and 14 aging days. The coated film exhibited an increase in water vapor barrier property with increasing aging time. It was suggested to the physical and chemical reaction in coated film, which continued throughout aging at an ambient temperature due to deficient curing (Bang and Kim, 2012).

2.7.3 X-ray diffraction (XRD)

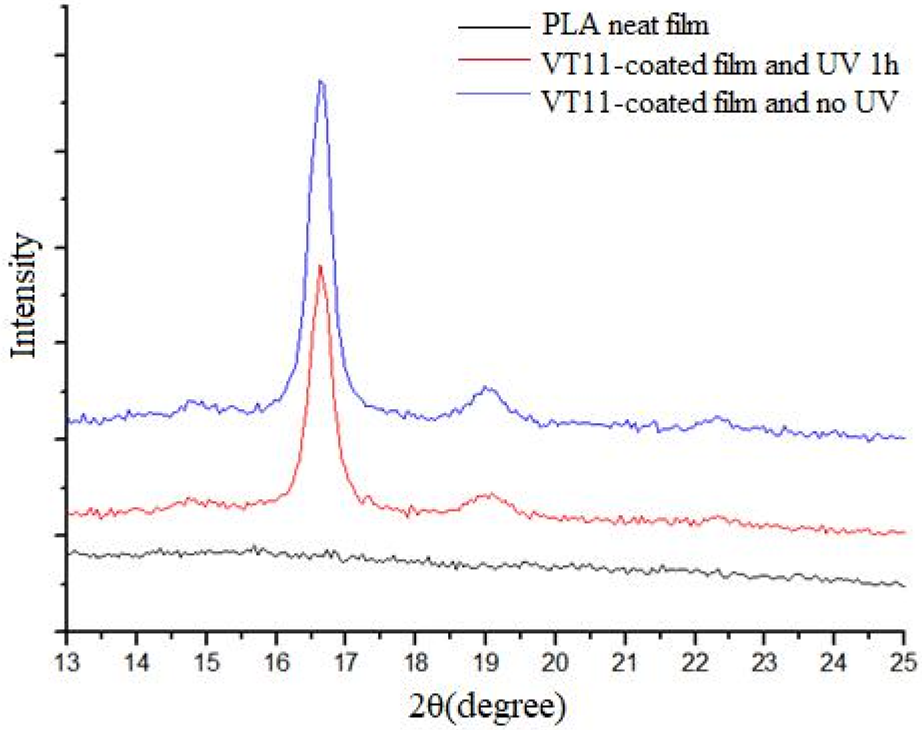


Figure 21 X-ray diffraction patterns for the PLA neat film and VT11-coated film before and after UV-irradiation

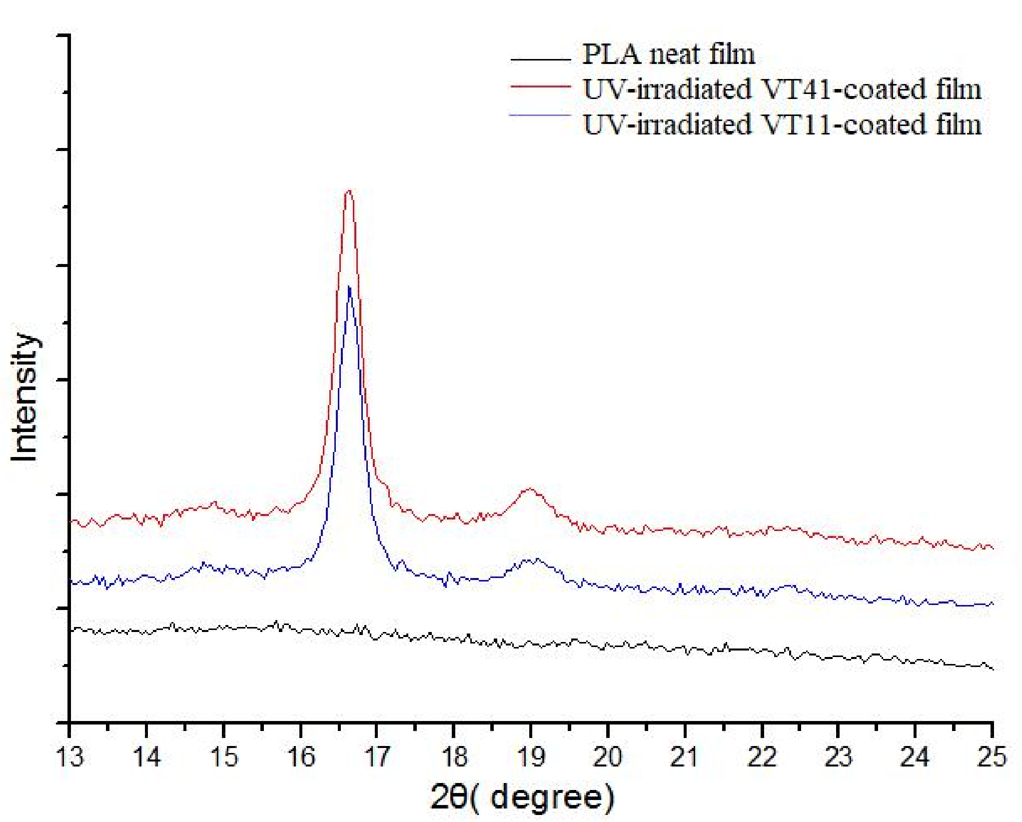


Figure 22 X-ray diffraction patterns for the UV-irradiated VT41-coated film and VT11-coated film in comparison with PLA neat film

UV- irradiation and the different mole ratio of VTES and TEOS could change the structures of coating films. These also possible to change its crystalline structures and crystallinities. VT11-coated film and VT41-coated film were selected to be investigated by XRD testing, because of these structures could be changed a lot after UV-irradiation and also affected by the content of TEOS. VT14-coated film was found no changes in structure after UV-irradiation by FTIR testing (Figure 19), due to a small number of C=C bonds in VT14-coated film.

Figure 21 shows the XRD patterns for the PLA neat film and VT11-coated film before and after UV-irradiation. The neat PLA matrix was amorphous, due to a scattered intensity distribution XRD curve with a broad maximum was observed for PLA neat film at 2θ = 16.6°. The broadest peak of PLA neat film was ascribed to reflections from (2 0 0) and/ or (1 1 0) planes, while less intense peaks were also observed at 2θ= 14.7, 18.9, and 22.2°, respectively, corresponding to reflections of (0 1 0), (2 0 3), and (0 1 5) planes (Yasuniwa *et al.*, 2006). It was found that coated-PLA films showed peaks at the same 2θ values as PLA neat film. This was indicated that the presence of silica particle and the UV-irradiation did not change the crystalline structure of PLA matrix. However, crystallinity of VT11-coated film had a significant increase in comparison with PLA neat film, due to the dispersed nanosized silica particles, which formed from sol–gel reactions, appear to act as effective nucleating agents, and the crystallization rate was promoted. The same result was also found by Bang and Kim, 2012. Actually, PLA/ clay nanocomposites were also observed the similar crystallization behavior. The crystallization rate of PLA/ clay nanocomposites was increased due to nanoclay had large surface area and provided more nucleating site (Chow and Lok, 2009; Lewitus *et al.*, 2006). Nevertheless, crystallinity of VT11-coated film was decreased after UV-irradiation for 1h. It suggested that the molecular chain's mobility of UV-irradiated VT11 coating films was restricted due to strong phase attraction. The lower molecular chain's mobility of UV-irradiated VT11 coating films could retard the regular packing into crystal lattices and decreased the crystallization rate.

On the other hand. Figure 22 shows the X-ray diffraction patterns for the UV-irradiated VT41-cotaed film and VT11-coated film in comparison of PLA neat film. VT11-coated film and VT41-coated film exhibited the same 2θ positions crystalline peak as PLA neat film, basically maintaining the α-form crystals. It proved that the presence of silica did not change the crystalline structure of PLA matrices. A lower peak intensity and area of VT41-coated film were observed than VT11-coated film, due to the higher content of VTES provided a larger number of C=C bonds and performed the vinyl polymerization. It had a restriction for the molecular chain's mobility of VT41-coating films, the crystallinity was decreased.

2.7.4 Oxygen transmission rate (OTR)

The oxygen barrier property is very important factor for a packaging to keep food as fresh. The oxygen permeability coefficient (OPC) is a parameter to quantify the oxygen barrier property which indicates the amount of oxygen that permeates per unit of area and time ($cc.m.m^{-2}.s^{-1}.Pa^{-1}.10^{-11}$).

Together with the permeability coefficient and the oxygen transmission rate (OTR), expressed in cc/m^2 s, is given. The OPC is correlated to the OTR by the following:

$$\mathrm{OPC} = \frac{OTR{*}l}{\Delta P} \quad \text{(Huglin and Zakaria., 1983)}$$

where l is the thickness of the film, and ΔP is the difference between oxygen partial pressure across the film [Pa]. $\Delta P = P_1 - P_2$, where P_1 is the oxygen partial pressure at the temperature test on the test side, and P_2 is equal to zero on the detector side.

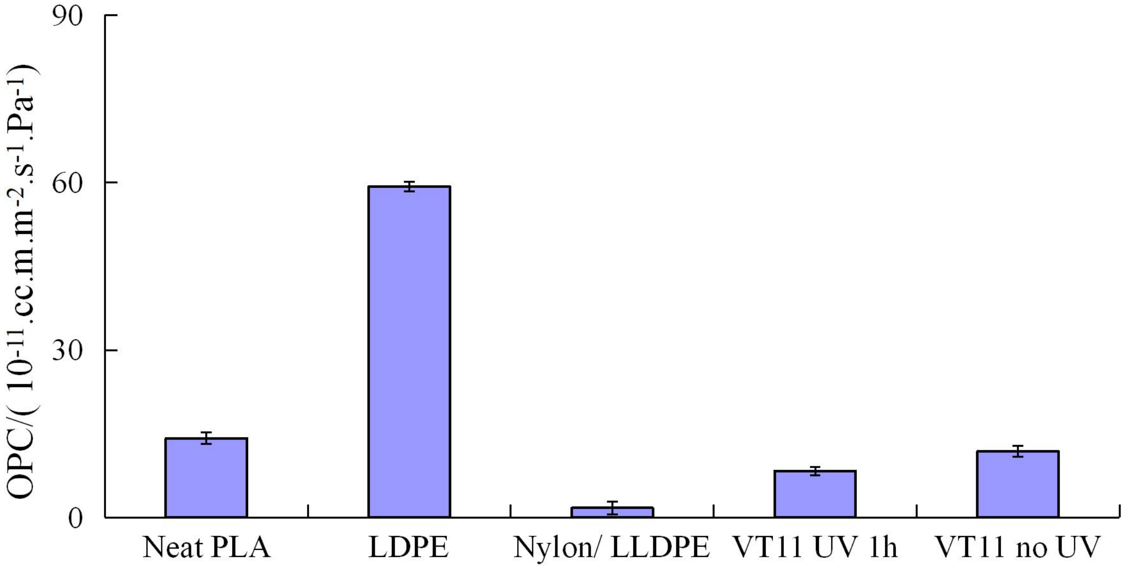


Figure 23 The oxygen permeability coefficient of VT11-coated film before and after UV-irradiation in comparison with PLA neat film, LDPE film and nylon/ LLDPE film

Figure 23 shows the OPC of VT11-coated film before and after UV-irradiation in comparison with PLA neat film, LDPE film and nylon/ LLDPE film. Nylon/ LLDPE showed the lowest OPC value by 1.724cc.m.m^{-2}.s^{-1}.Pa^{-1}.10^{-11}. VT11-coated film had a lower OPC value than LDPE film and PLA neat film. In particular, the OPC value of UV-irradiated VT11-coated film and VT11-coated film and without UV-irradiation were decreased 24.8% and 41.2%, respectively, compared with PLA neat film. It indicated that the oxygen barrier property of PLA film was enhanced by coating the gel on the surface. The dense silica structure could provide a great barrier to oxygen. On the other hand, it also showed that the OPC value of VT11-coated film was increased by 29.7% after UV-irradiation for 1 h. Because the crystallinity of VT11-coated film had a decrease after UV-irradiation (as shown in XRD testing). As reported from Kofinas *et al*., 1994, gas molecules cannot permeate through the polymer crystallites, because gas molecules were insoluble into the material. Thus, the reduction of crystallites permeability was due to the decrease in available volume of polymer for gas penetration and to a large tortuous path between the crystallites (Jenkins *et al*., 1992).

2.7.5 Water contact angle

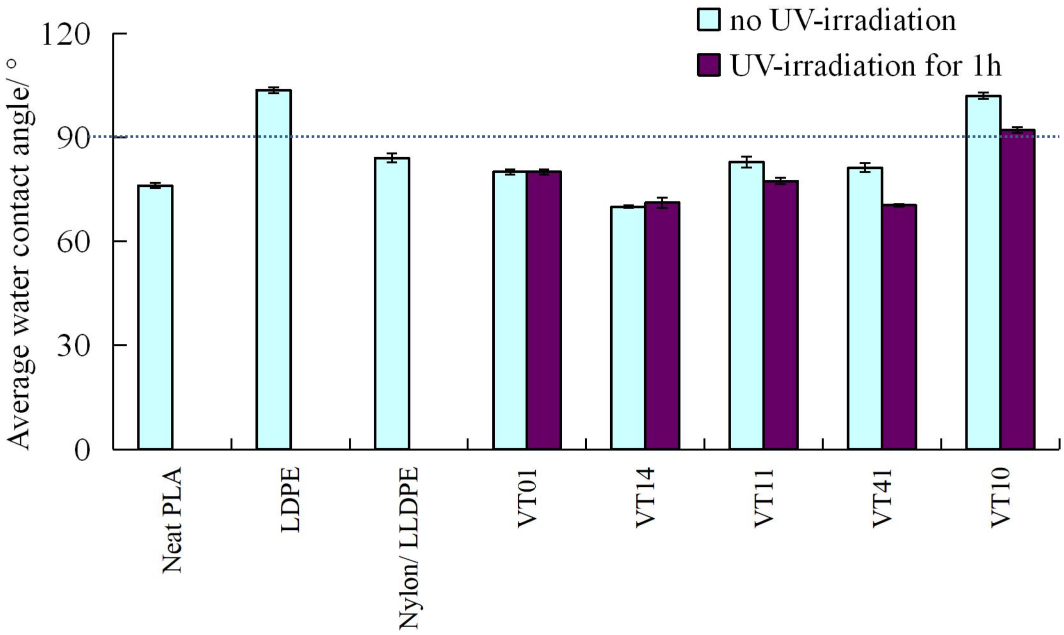
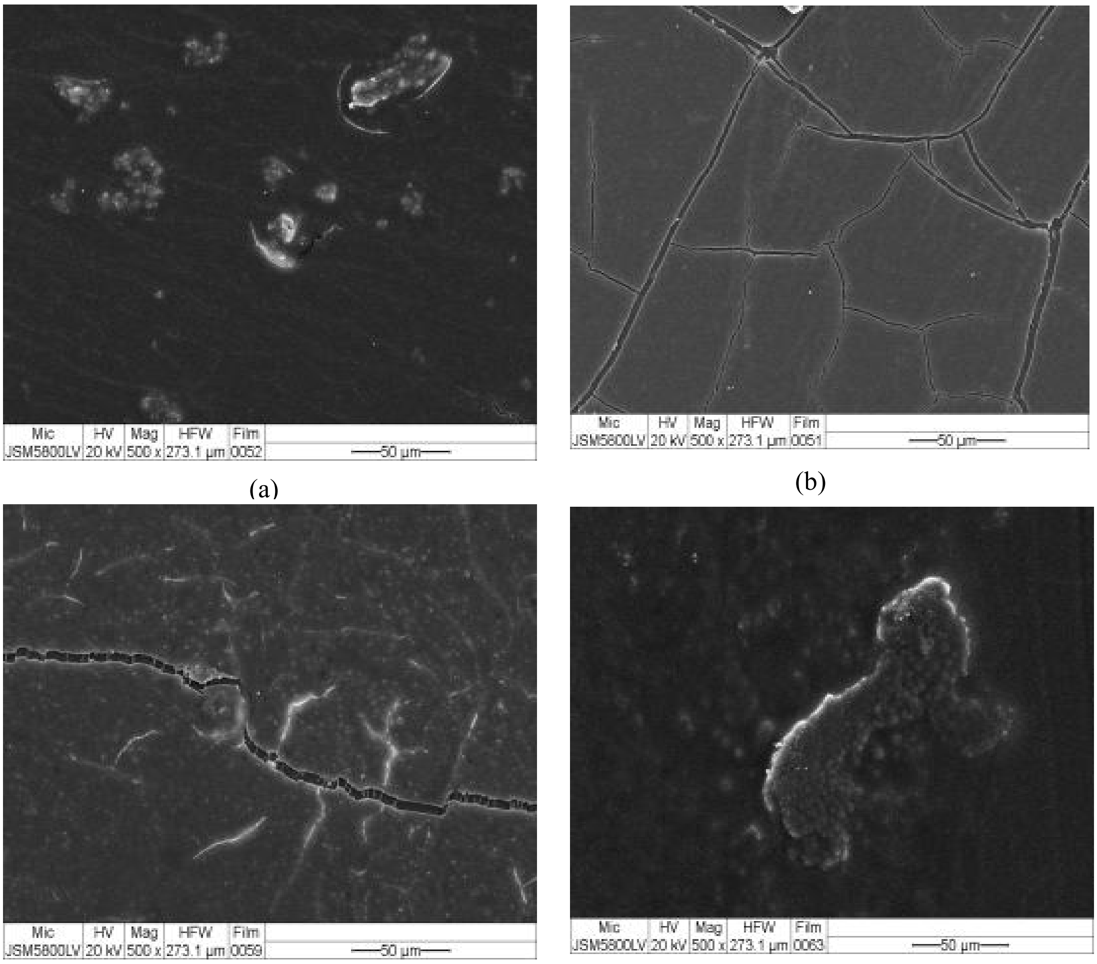


Figure 24 The average water contact angle of coated films in comparison with PLA neat film, LDPE film and nylon/ LLDPE film

Water contact angle is a significant parameter to investigate the wettability of materials. Generally, a water contact angle less than 90° corresponded to the surface of the coated film favoring wetting, and a water contact angle more than 90° corresponded to the low wettability (Yuan and Lee, 2013). In Figure 24, LDPE film had the highest water contact angle by 103.59°, due to LDPE had a hydrophobic surface (Li et al., 2012). Nylon/ LLDPE film had a little bit higher water contact angle than PLA neat film and lower than LDPE film. Moreover, most of coated films presented low water contact angle (<90°), which demonstrated that coated films possessed good wettability. Because hydrophilic hydroxyl groups (-OH) on the surface of coated films. Another reason for the low water contact angle of coated films could be ascribed to the presence of residual solvent medium, water (H_2O) and alcohol (CH_3OH, and C_2H_5OH), which formed by the acid-hydrolysis of TEOS and VTES. The hydrophilic bond (OH) in C_2H_5OH could be embedded in the coating materials and decreased water contact angle (Wang *et at*., 2012). Latthe *et al*., 2010 was indicated that the surface of silica film covered with fewer silicon alkyl groups exhibit low water contact angle, because of the by-product of alcohol was formed by the acid-hydrolysis of precursor. However, VT41-coated film and VT10-coated film had a relatively high water contact angle (>90°), which corresponded to low wettability. Because carbon double bond (C=C) was hydrophobic group and there were a lot of C=C bonds in these materials. On the other hand, the amount of C=C bond in coated films was reduced after UV-irradiation by performing the vinyl polymerization. Thus, water contact angle of coated film for VT41, VT10 and VT11 had a decrease by 10.8%, 11.4% and 6.6%, respectively, after UV-irradiation for 1h. The water contact angle of VT14-coated film did not have an obvious change due to it contained a small amount of C=C bond. These results were also observed in FTIR analysis.

2.7.6 Morphology

Phase morphology of coated films for VT11 with ICPTES, VT11 without ICPTES, VT14 and VT41 was showed on Figure 25. ICPTES was used as the silane coupling agent to bring interactions of PLA chain and silica matrix. In Figure 25(a) and Figure 25(b). It was clear to see that a few small cracks on the surface of VT11-coated film with ICPTES, but a lot of big cracks were found on the surface of VT11-coated film without ICPTES. These proved that ICPTES could promote the phase attraction and suppressed the phase separation. On the other hand. It was difficult to completely avoid cracks on surface of coated films, because water and the co-solvent of THF were very easy to evaporate to environment on drying process and the coated gel was shrinking and forming crackers. Moreover, a big crack and some small cracks were found on the surface of VT14-coated film (Figure 25(c)). It was indicated that less amount of VTES was also decreased the phase attraction of coated film due to a small number of C-C covalent bonds were formed. However, adding too much VTES would cause a disordered structure. It was observed that a lot of particles were aggregated together on the surface of VT41-coated film in Figure 25(d).



(a) (b)

(c) (d)

Figure 25 Phase morphology of coated film after UV-irradiation 1h. (a). VT11-coated film with ICPTES. (b). VT11-coated film without ICPTES. (c). VT14-coated film. (d). VT41-coated film

In addition, Figure 26 shows the morphology of surface and cross section of VT11 before and after UV-irradiation for 1h. A big crack on the surface of VT11-coated film without UV-irradiation and a small crack on the surface of UV-irradiated VT11-coated film were observed. It proved that the phase attraction was increased and the phase separation was further suppressed after UV-irradiation for 1h. Moreover, in Figure 26(b) and Figure 26(d), there was the similar thickness about 2μm of the coating gel.

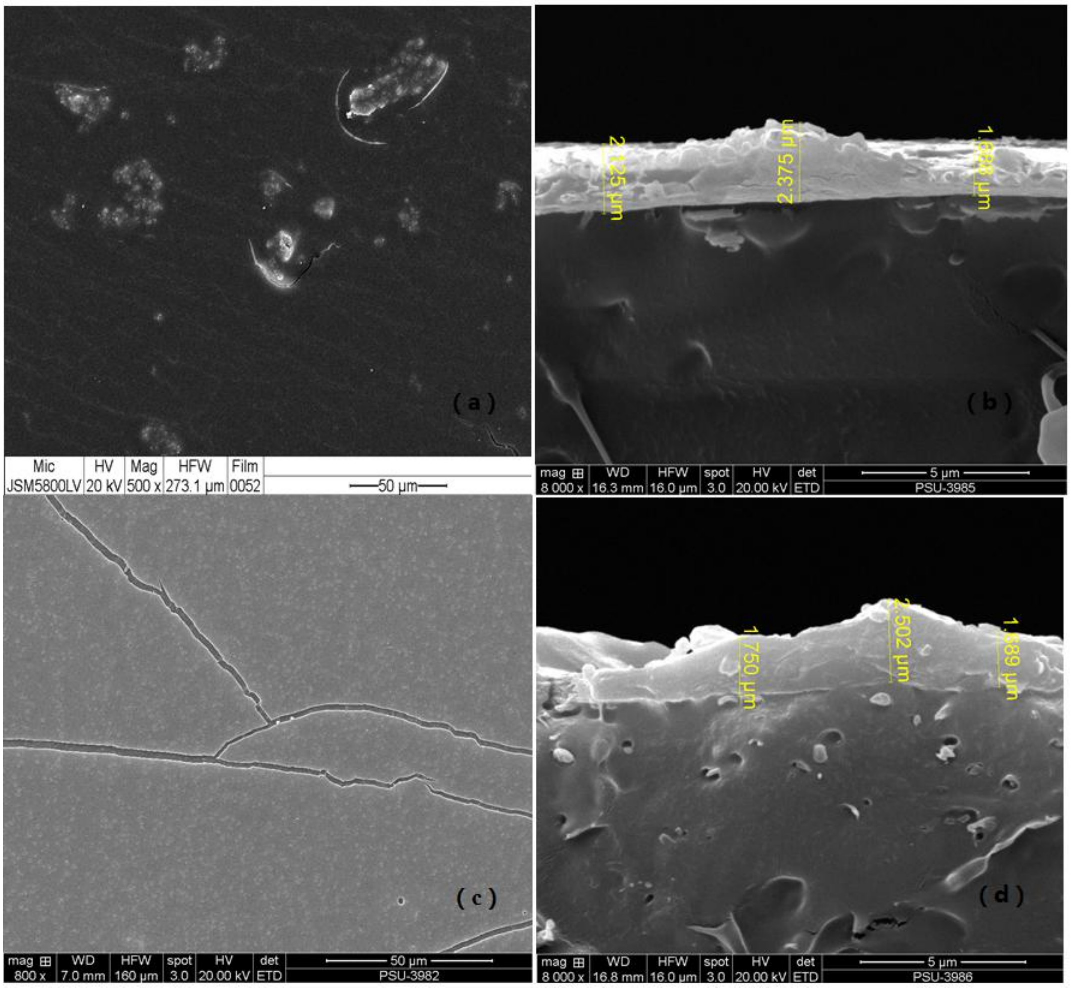


Figure 26 The morphology of surface cross section of VT11-coated film before and after UV-irradiation for 1h. (a), (b) The surface and cross section of VT11-coated film and UV-irradiation for 1h, respectively. (c), (d) The surface and cross section of VT11-coated film and no UV-irradiation, respectively

2.7.7 Atomic force microscopy (AFM)

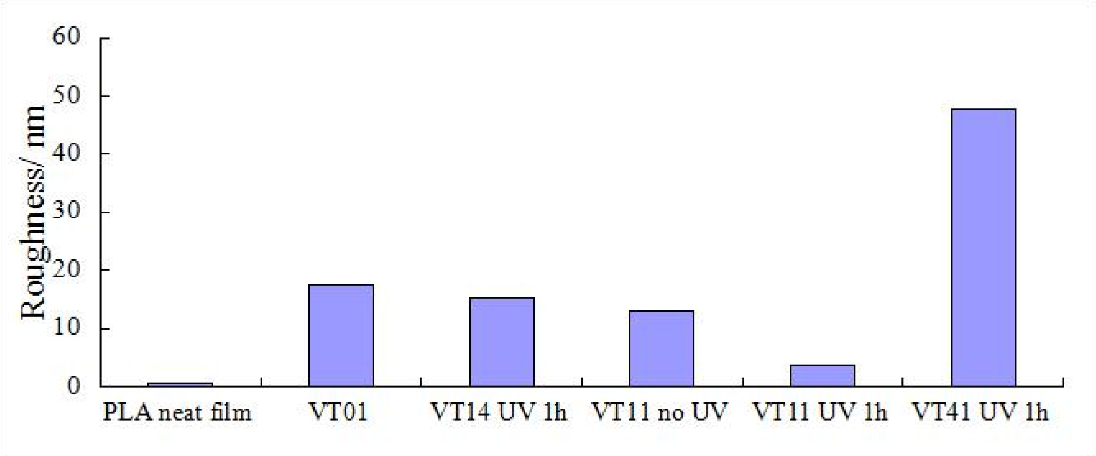


Figure 27 Surface roughness of UV-irradiated coated film for VT01, VT14, VT11 and VT41 in comparison with VT11-coated film without UV-irradiation and PLA neat film

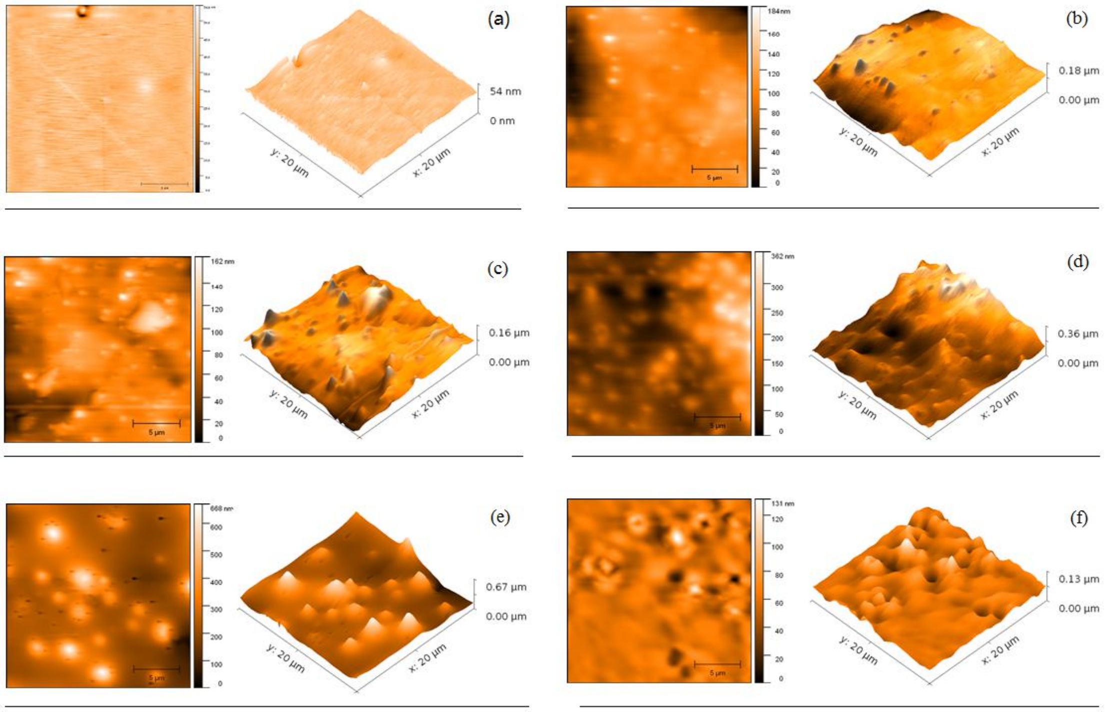


Figure 28 Surface topography of (a) PLA neat film, (b) VT01-coated film, (c) VT14-coated film, (d) VT41-coated film, (e) VT11-coated film, (f) VT11-coated film without UV-irradiation

Figure 27 and Figure 28 show the surface roughness and surface topography of UV-irradiated coated film for VT01, VT14, VT11 and VT41 in comparison with VT11-coated film without UV-irradiation and PLA neat film, respectively. PLA neat film had the lowest value of surface roughness. However, an increase values of surface roughness were observed after coating process. It suggested that the coated gel was not homogenous on the surface of substrate because of the shrinkage and the evaporation of water as well as THF solvent on drying process. Moreover, the value of surface roughness of VT11-coated film decreased by 31.2% after UV-irradiation. It indicated that UV-irradiated VT11-coated film was rather smooth. UV-irradiated VT41-coated film had the highest values of surface roughness, compare with other samples. Figure 28(d) further presented a rough surface of UV-irradiated VT41-coated film with unevenness of larger than a few nanometers and with small grains of 20 to 50nm in diameter. Because a high amount of VTES would cause a disordered structure, the small particles were aggerated together. These results were also proved by SEM testing. UV-irradiated coated films for VT10 and VT14 had a little higher values of surface roughness than UV-irradiated VT11-coated film. Nevertheless, all coated films were still not rough enough to affect the water contact angle (Petcu et al., 2015), especially for the UV-irradiated VT11-coated film.

2.8 Conclusions

PLA and silica hybrid coated films were synthesized. Oxygen and water vapor barrier properties of coated-PLA films were promoted by adding silane coupling agent ICPTES and performing UV-irradiation for 1h, due to strengthen the phase attraction and the stability of microstructure. The mole ratio of VTES/ TEOS had a significant impact on the barrier property of coating material. Value of WVP for UV-irradiated VT11-coated film was decreased by 24.6% in comparison with PLA neat film. A lower oxygen permission coefficient for VT11-coated film was also observed than PLA neat film and LDPE film. Moreover, SEM imagine showed no phase separation on the surface and cross-section of UV-irradiated VT11-coated film. AFM testing also proved that UV-irradiated VT11-coated film was rather smooth. In addition, VTES had an effect on the water contact angle of the coated film, due to C=C was a hydrophobic grope. As a result, UV-irradiated VT11-coated film had the best properties in comparison with coated films for VT01, VT14, VT41, VT10 and PLA neat film, but its barrier properties still lower than nylon/ LLDPE film. On the other hand. WVP of UV-irradiated VT11-coated film was found decreased with aging time going, due to dense network structures were continuously generated after drying.

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CHARPTER 3

QUALITY CHANGES OF SHRIMP CRACKERS PACKAGED IN COATED-PLA POUCH DURING STORAGE

3.1 Abstract

Chemical and physical changes of fried shrimp cracker stored during storage of 56 days at room temperature were investigated. The shrimp cracker stored in coated-PLA film have a lower increasing rate of moisture content than stored in PLA neat film during storage. Lower peroxide value (PV) and thiobarbituric acid reactive substances (TBARS) value were observed for shrimp cracker stored in coated-PLA film than that stored in LDPE film and PLA neat film. These indicated that coated-PLA film could decrease the rate of lipid oxidation for shrimp cracker and it was more effective than PLA neat film and LDPE film. All samples had a decrease crispiness and an increase toughness during the 56 days of storage. Moreover, pH of all samples was increased up to 56 days of storage. The control sample and shrimp cracker stored in PLA neat film exhibited higher pH value than others. Overall, coated-PLA film could be an alternative to maintain the chemical and physical qualities of shrimp cracker.

3.2 Introduction

Shrimp crackers, commonly known as *krupuk*, are a popular food in China, Indonesia, and Thailand. In deep immersion oil frying, the sample receives heat contact from all directions resulting in quick volume expansion and a uniform and larger size. In addition, a porous structure is formed and the final fried cracker provides high-quality softness, crispiness and improved volume expansion (Nguyen *et al*., 2013). However, due to the porous structure, shrimp cracker is very sensitive to the moisture. The crispiness is decreased with moisture absorption. Nilsuwan *et al*., 2016 indicated that the decrease in crispness and increase in moisture content for shrimp crackers during 15 days of storage. In particular, Sirpatrawan 2009 found that crisp snack foods would lose the crispness if moisture content reached 0.068g/g (Dry basis). Moreover, after drying and baking of the crackers, oil is prayed to them for flavor adherence. This residual oil eventually contributes to rancidity of the product (Gunaratne, *et al*., 2015). These problems led the researchers to examine the use of different packaging systems to decrease the rate of deterioration.

PLA film is currently one of the most attractive packaging materials, because of it attracts lots of good properties, such as good mechanical properties, good biocompatibility and biodegradability. Nevertheless, PLA film has low barrier properties compared with conventional petroleum-based materials. One of the common approaches to solve this problem is to synthesis organic-inorganic hybrid coating materials. Bang and Kim, 2012 and Lotti *et al*., 2009 indicated that organic-inorganic hybrid coating materials based on PLA films were effective to promote the resistance to oxygen and water vapor permeation.

Thus, in this study, we reported a novel strategy to synthesize organic-inorganic hybrids by sol-gel method and its application as coating materials for PLA film. The quality changes of shrimp crackers stored in coated-PLA film during the extended storage in comparison with PLA neat film, LDPE film and nylon/ LLDPE film were also investigated.

3.3 Materials and chemicals

3.3.1 Preparation of coated-PLA film

Tetraethyl orthosilicate (TEOS, Aldrich, 99%) was used as an inorganic silicate precursor. 3-Isocyanatopropyltriethoxysilane (ICPTES, Shanghai Aladdin Biochemical Technology Co., Ltd., 95%) and Triethoxyvinylsilane (VTES, Shanghai Aladdin Biochemical Technology Co., Ltd., 97%) were used as silane coupling agents to strengthen phase attraction. Benzoin Isobutyl Ether (BIE, Zhejiang

Maya-Reagent Co., Ltd., 95%) was used as a photoinitiator to promote the photo-polymerization rate. PLA resin (PLA 2002D, NatureWorks LLC) was used as an organic part in the hybrid materials. Hydrocholoric acid (HCl, Loba chemie 35.4%) was used as catalyst to promote hydrolyze reaction rate. Moreover, Tetrahydrofuran (THF, RCI labscan, 99.8%) was used as co-solvent. The thickness of PLA substrate film was 30±2 μm.

3.3.2 Investigation for quality changes of shrimp cracker

Dried shrimp cracker was bought from a market in Hat Yai, Songkhla, Thailand. Palm oil was bought from OLEEN Company Limited (Bangkok, Thailand).

Trichloroacetic acid and iron (II) chloride was obtained from Merck (Darmstadt, Germany). Cumene hydroperoxide and thiobarbituric acid was procured from Fluka (Buchs, Switzerland). Methanol, chloroform and ammonium thiocyanate was obtained from Lab-Scan (Bangkok, Thailand). All chemicals were analytical grade.

3.3.3 Equipment

Table 14. Equipment used for investigating the quality changes of shrimp cracker

Instruments	**Model**	**Company**
Colorimeter	Hunter lab, colorflex	Hunter Associates Laboratory, INC, USA
Environmental chamber	KBF 115	Binder, Germany
Homogenizer	T25B	IKA, Germany

Table 14 (Continued)

Instruments	**Model**	**Company**
Impulse sealer	ME-300HIM	S.N.MARK Ltd., Thailand
Microfluidics homogenizer	HC-5000	Microfluidizer, USA
Refrigerated centrifuge	Allegra 25R	Beckman coulter, USA
Spectrophotometer	UV- 1800	Shimadzu Corporation, Japan
Texture analyzer	TA-XT2	Stable Micro Systems, UK
Water bath	WB 14	Memmert, Germany
Magnetic stirrer	RO 10 power	KIKAL labortechnik, Germany

3.3.4 Experiment

3.3.4.1 Preparation of coated-PLA film

PLA/Siloxane hybrid coating materials were prepared by sol-gel method. First, a mixture of (VTES and TEOS)/H_2O/THF at mole ratio of 1:2:6 were stirred for 3 h to hydrolyze the VTES and TEOS at room temperature. Hydrocholoric acid was used as catalyst to increase the reaction rate, as well as to adjust the pH of to 2, as the rate of hydrolysis reaction was promoted in acidic condition. The composition of the solution was VTES: TEOS at mole ratio of 1:1 (VT11). The total mole of TEOS and VTES was 0.03 mol. Second, PLA resin was dissolved in THF solvent to obtain 5 wt% PLA solutions with homogeneous dispersion. Moreover, 0.001 mol ICPTES was used to modify PLA resin, and stirred for 3 h at 60°C. The partially hydrolyzed inorganic siloxane precursor was mixed with modified PLA and stirred for 3 h at room temperature. Finally, 0.001 mol benzoin isobutyl ether was added to the solution with the VTES/ BIE molar ratio of 5/100 as a photoinitiator. The solution was further stirred for 1h.

The resulting gel was coated on PLA films using a bar coater (F99000, Feldham 2, Austriag). The coating films were aged and put in a closed package with silica gel for 12h. Then the samples were irradiated under UV light at 30000lux for 1 h. Moreover, the control sample was prepared without UV irradiation. Finally, all samples were dried in a drying oven at 60°C for 24h.

3.3.4.2 Investigation for film properties

3.3.4.2.1 Thickness

The thickness of coated-PLA film, PLA neat film, LDPE film, nylon/ LLDPE film was measured by using micrometer.

3.3.4.2.2 Water vapor permeability (WVP)

WVP of coated-PLA film was measured by using a modified ASTM method (ASTM, 1989). PLA neat film, LDPE and nylon/ LLDPE films were used as references. Briefly, the coated-PLA films and the reference films were cut to the diameter of 7.5 cm circles and their thickness were measured. Each sample was put on the permeability cups (Alumina cups) which contain enough dried silica gel (0% RH) and measuring their weight. Finally, all samples were placed in environmental chamber at 25 °C and 50% RH, and the weight of each sample should be recorded every day until one week. WVP was calculated by using the equation:

$$\text{WVP}\ (\text{gm}^{-1}\text{s}^{-1}\text{Pa}^{-1}) = \text{wlA}^{-1}\text{t}^{-1}(\text{P}_2 - \text{P}_1)^{-1}$$

Where w is the weight gain of the cup (g); l is the film thickness (m); A is the exposed area of film (m^2); t is the time of increase (s); P_2 - P_1 is the vapor pressure difference across the film (Pa).

3.3.4.2.3 Oxygen transmission rate (OTR)

OTR of coated-PLA film was tested by using an oxygen transmission rate tester according to ASTM standard D3985. PLA neat film, LDPE and nylon/ LLDPE films were used as references. The test temperature was set to 23 °C and the RH was set to 0% relative humidity. The test area of coated PLA films and the reference film were considered 50 cm^2. While measuring the sample, the film was separated into two chambers in a permeation cell, pure oxygen was passed on the upper side of the sample film, and pure nitrogen was passed on the lower side of the sample film. Oxygen was permeated into nitrogen part through the film. OTR values were obtained from the instrument.

3.3.4.3 Preparation of fried shrimp cracker

The diameter of dry shrimp cracker was 5 mm and the thickness was 1.5 mm. Samples was fried with palm oil until completely puffed, and then shrimp crackers obtained was placed on the frying basket drain the oil for 10 mins and cool at room temperature before used.

3.3.4.4 Investigation for quality changes of shrimp cracker

10g shrimp cracker was placed into heat-sealed pouch from coated-PLA films. The pouch was heat-sealed and the seal was checked to ensure that there was no leakage. The samples were stored in at ambient condition (30 ± 0.5 °C and 65 ± 5 %RH). 10 g samples stored in low-density polyethylene (LDPE), nylon/ Linear low-density polyethylene (Nylon/ LLDPE) bag and neat PLA were prepared.

Sample placed in a plastic cup without sealing was also prepared. And then all samples were taken at 7 days, 14 days, 35 days and 56 days for analyses.

3.3.5 Characterization

3.3.5.1 Moisture content

The method of AOAC (2000) was used to measure the moisture content of shrimp cracker.

3.3.5.2 Determination of pH

Shrimp cracker (2g) were homogenized with 10 ml of distill water for 1 min at a speed of 5000 rpm. The mixture solution was stored at room temperature for 5 min, and then the pH was measured by using a pH-meter.

3.3.5.3 Determination of color

Color of shrimp crackers was measured by using a CIE colorimeter. A white standard (L* = 92.83, a* = 1.27 and b* = 0.52) was used to calibrate the colorimeter.

3.3.5.4 Measurement of textural properties

Textural property of shrimp cracker was tested by using a texture analyzer. Ottawa cell with flat square probe was used to determine the crispiness, in which the maximum force required to break the shrimp cracker samples was recorded. Toughness was determined by determining the area under the curve during compressing. The studies were conducted using a pre-test speed of 1.0 mm/s, test speed of 2.0 mm/s, distance of 5.0 mm, and load cell of 50 kg.

3.3.5.5 Measurement of thiobarbituric acid reactive substances (TBARS)

Shrimp crackers (5g) were added with 25ml of distilled water. The mixtures were homogenized at a speed of 13,500 rpm for 2 min, and the mixture was transferred in to a 250ml conical flask containing 23.5ml of distilled water. Thereafter, 1.25ml 6mol/l HCl were added to adjust the pH to 1.5, and then 4-5 glass beads were added in to the mixture before heating using an electric mantle. Distillation was performed until the distillate of 25 ml was obtained. An aliquot (2.5ml) of distillate was placed in a glass-stoppered tube, and 2.5 ml of TBA reagent was added. The mixture was heated in boiling water for 35 min. After heating, the reaction mixture was cooled in water for 10min and the absorbance at 532 nm (A_{532}) was measured. TBARS=7.8*A_{532} (Xiong *et al*., 2015).

3.3.5.6 Measurement of peroxide value (PV)

Shrimp cracker (1g) was mixed and homogenized with 11 ml of chloroform/methanol (2:1, w/v) at speed of 13,500 rpm for 2 min, and then the What man No.1 filter paper was used to filter the mixture solution. 2ml 0.5% NaCl solution was added to 7 ml of the filtrate. The mixture was separated to two phases by centrifuging at speed of 3000×g for 3 min. The 3ml solution at lower phase was mixture with 2ml cold chloroform/methanol (2:1, w/v) solution. Moreover, 25 μl ammonium thiocyanate and 25 μl iron (II) chloride were added and reacted in the mixture solution for 20mins at room temperature (Shantha and Decker, 1994). Finally, the absorbance at 500nm was measured. Cumene hydroperoxide was used to prepared the standard curve at a concentration range of 5-25 ppm.

3.3.6 Experimental result and discussion

Table 15 Thickness, water vapor permeability (WVP) and oxygen permeability coefficient (OPC) of films from coated-PLA film, PLA neat film, low density polyethylene (LDPE) film and nylon/linear low-density polyethylene (Nylon/ LLDPE) film

Films	Thickness(mm)	WVP (10^{-13} g.m.s^{-1}.m^{-2}.Pa^{-1})	Oxygen permeability coefficient/ 10^{-11}.cc.m.m-^{2}.s^{-1}.Pa^{-1}
LDPE	0.032±0.001	6.69±0.15	59.28±1.03
Nylon/ LLDPE	0.075±0.001	3.1±0.81	1.72±0.82
PLA neat	0.036±0.002	125.58±1.18	14.19±1.16
Coated-PLA	0.029±0.001	95.2±1.78	11.86±0.75

Table 15 shows the values of thickness, WVP and OPC of coated-PLA film, PLA neat film, LDPE film and nylon/ LLDPE film. Different films had various properties. Film from nylon/ LLDPE showed the highest thickness, while coated-PLA film showed the lowest thickness. Moreover, nylon/ LLDPE film had the lowest values of WVP and OPC, coated-PLA film showed lower values of WVP and OPC than PLA neat film. LDPE film had a good water vapor barrier property, but it showed the highest values of OPC. Overall, nylon/ LLDPE film had the best oxygen and water vapor barrier properties. Moreover, it proved that barrier properties of PLA neat film could be promoted by the coating process. All of values of WVP and OPC were normalized.

3.3.6.1 Moisture content

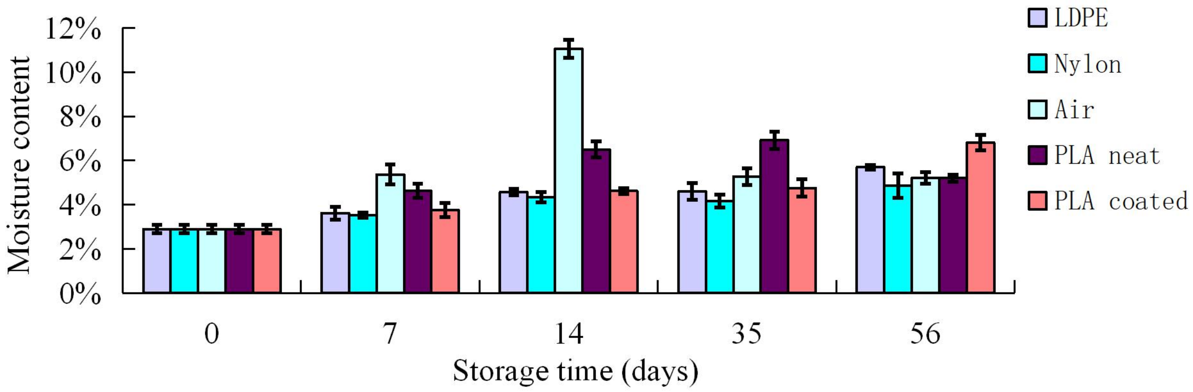

Figure 29 Moisture content of shrimp cracker stored in coated-PLA film, PLA neat film, LDPE film and nylon/ LLDPE film during 56 days of storage at 30 ± 0.5°C and 65 ± 5 % RH in comparison with the control (Fried shrimp cracker without packaging)

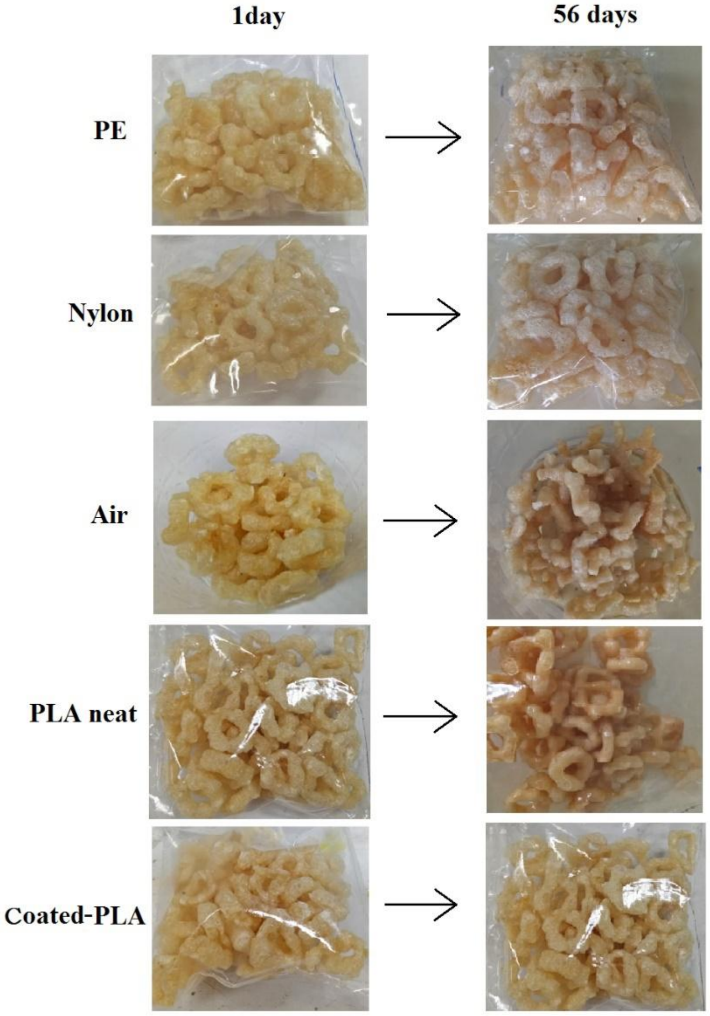

Figure 30 The morphology changes of samples at first day in comparison with the day 56 of storage

Moisture content changes of shrimp cracker stored in coated-PLA film, PLA neat film, LDPE film and nylon/ LLDPE film during 56 days of storage in comparison with the control (Fried shrimp cracker without packaging) are depicted in Figure 29. The initial moisture content of the fried shrimp cracker was measured at 2.90%. It was found that the moisture content of shrimp cracker for all samples increased up to 14 days of storage. Moisture content of shrimp cracker stored in PLA neat film and control sample have a sharp growth by 55.4% and 73.8% at the day 14 of storage, respectively, as compared with the initial moisture content of the fried shrimp cracker. Nevertheless, the decrease of moisture content of the shrimp cracker stored in PLA neat film and control sample was observed after 14 days of storage, due to some water in the shrimp cracker evaporated to environment (Nilsuwan *et al*., 2015). Moreover, the moisture content of shrimp cracker stored in coated-PLA film, LDPE film and nylon/ LLDPE film have a stable growth by 57%, 49% and 40%, respectively, at the day 56 of storage, as compared with the initial moisture content in the fried shrimp cracker.

Figure 30 shows the morphology changes of shrimp cracker stored in coated-PLA film, PLA neat film, LDPE film, nylon/ LLDPE film and control sample at the first day in comparison with at the day 56 of storage. The shape of shrimp cracker stored in nylon/ LLDPE film and LDPE film just have a small change, but the volume of control sample and shrimp cracker stored in PLA neat film have a significant shrinkage and return to the original small shape (Without fried) at the day 56 of storage. The shrimp cracker became very hard and it had low moisture content. The shape of shrimp cracker stored in coated-PLA film also had a big changed, but it was found that the shrimp cracker had porous structure (Figure 30) and high moisture content (Figure 29). All of these results therefore confirmed that the shrimp cracker stored in nylon/ LLDPE film has the lowest moisture content throughout the storage. It was corresponded to the higher water vapor barrier property of nylon/ LLDPE film than LDPE, PLA neat film and coated-PLA film (Table 14). Moreover, coated-PLA film could be proved that it had a higher water vapor barrier property than PLA neat film, this result was also in accordance with the lower WVP of coated-PLA film in comparison with PLA neat film (Table 14).

3.3.6.2 pH

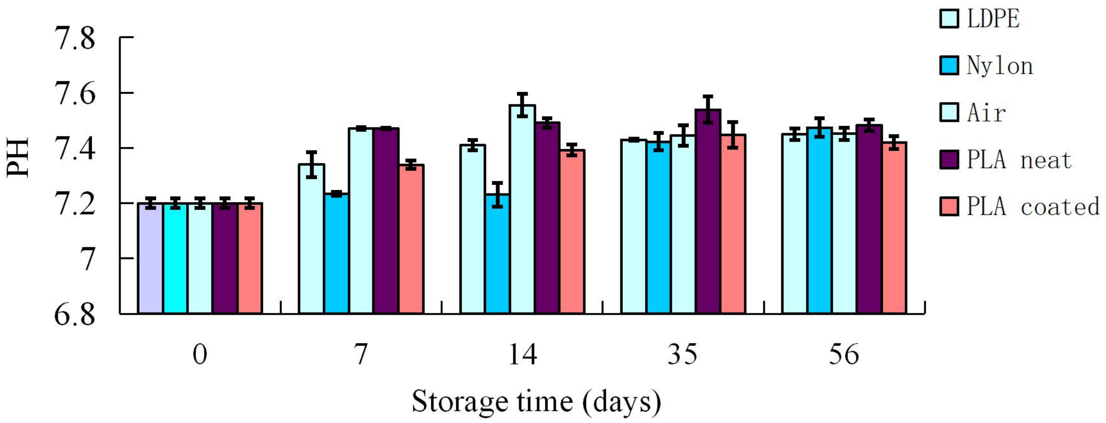

Figure 31 pH of shrimp cracker stored in coated-PLA film, PLA neat film, LDPE film and nylon/ LLDPE film during 56 days of storage at 30 ± 0.5 °C and 65 ± 5 % RH in comparison with the control (Fried shrimp cracker without packaging)

pH of shrimp cracker stored in coated-PLA film, PLA neat film, LDPE film and nylon/ LLDPE film during 56 days of storage in comparison with the control (Fried shrimp cracker without packaging) is shown in Figure 31. pH of all samples was increased up to 56 days of storage. These might be related to the decomposition of the volatile base compounds in shrimp cracker during storage (Lopez-Caballero *et al*., 2007). However, the control sample and shrimp cracker stored in PLA-neat film have a sharp growth of pH-value during 14 days of storage, due to high moisture content in the shrimp cracker (See Figure 29). The high moisture content could promote the microbial growth rate, especially the spoilage bacteria was related with increased decomposition of nitrogenous compounds (Nilsuwan *et al*., 2015). Moreover, the pH-value of the shrimp cracker stored in nylon/ LLDPE film exhibited a small change in first two weeks of storage, due to relatively low moisture content in the shrimp cracker. Shrimp cracker stored in LDPE film shows a similar pH-value with coated-PLA film. It might be ascribed to LDPE film have lower resistance to oxygen than coated-PLA film. High oxygen content in the pouch could increase the microbial growth rate and accelerate the changes of pH-value for shrimp cracker.

3.3.4.3 Textural properties

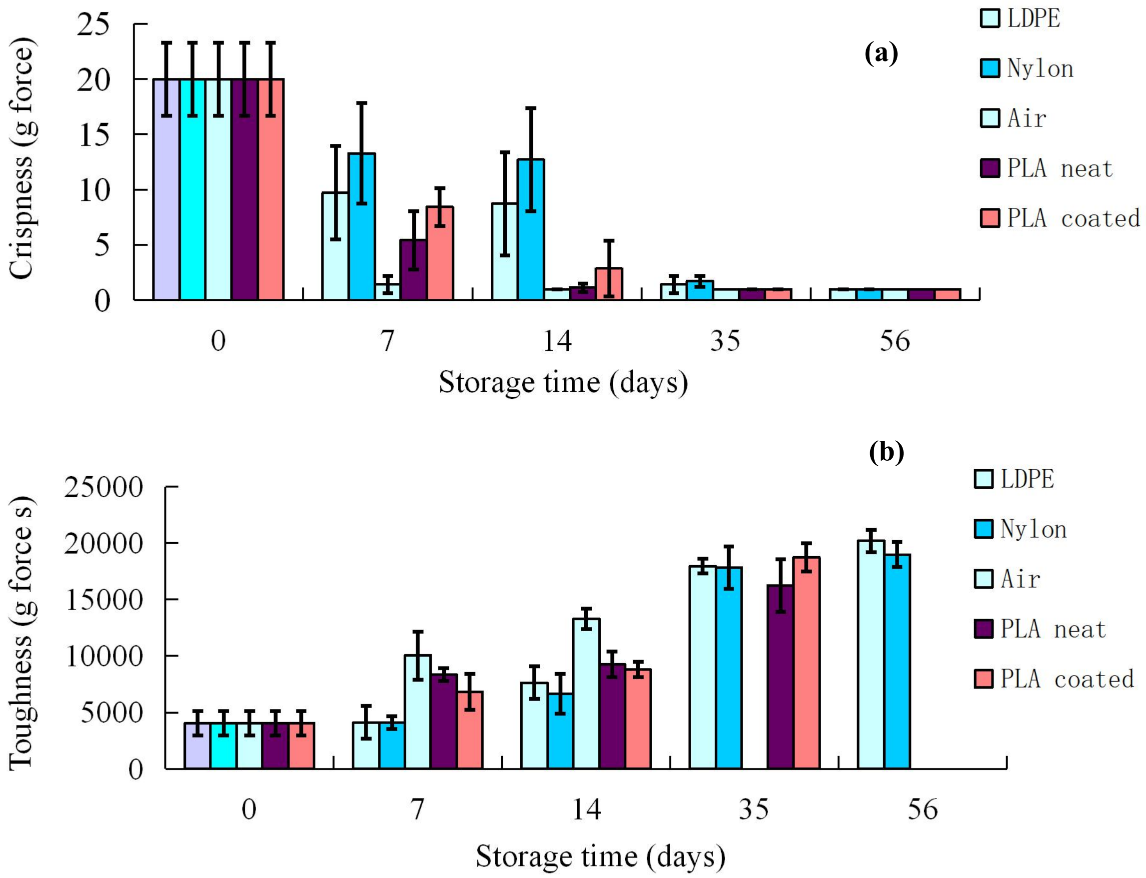

Figure 32 Crispiness (a) and toughness (b) changes of shrimp cracker stored in coated-PLA film, PLA neat film, LDPE film and nylon/ LLDPE film during 56 days of storage at 30 ± 0.5°C and 65 ± 5 % RH in comparison with the control (Fried shrimp cracker without packaging)

Crispiness and toughness changes of shrimp cracker stored in coated-PLA film, PLA neat film, LDPE film and nylon/ LLDPE film during 56 days of storage compared with shrimp cracker without packaging) are showed in Figure 32a and Figure 32b, respectively. Generally, the texture property of fried food was affected by the shrinkage and porosity, density (Ziaiifar *et al*., 2010). Fried shrimp cracker had high porous structure and provided good crispiness for shrimp cracker (Nguyen *et al*., 2013). In Figure 32a, all samples showed high crispiness at first day of storage, and the shrimp cracker was gradually lost crispiness during 56 days of storage. Particularly, the control sample had a sharp growth of crispiness by 92.9% during the first week of storage, due to high moisture was absorbed and the porous structure was broken. Shrimp cracker stored in coated-PLA film has lower decrease rate of crispiness than stored in PLA neat film. The crispiness of shrimp cracker stored in coated-PLA film and PLA neat film was decreased by 83.4% and 94.7% at day 14 of storage, respectively. This result was corresponded to coated-PLA film with higher barrier properties than PLA neat film. Moreover, it was found that nylon/ LLDPE film and LDPE film were more effectively to keep the shrimp cracker with high crispiness than others. One reason was ascribed to the good barrier properties of these films. Another reason might be related to the sharply shrinkage of shrimp cracker, which stored in coated-PLA film, PLA neat film and the control, during storage.

In Figure 32b. The toughness of all samples was increased during 56 days of storage, due to the moisture content in shrimp cracker was increased. Because the cracker had a higher extent surface when the water vapor contacted, and the structure of shrimp cracker might be fluidized by the water, the toughness was increased (Nilsuwan *et al*., 2016). However, no difference in toughness of shrimp cracker stored in nylon/ LLDPE film and LDPE film, due to the good water vapor barrier properties. It was also found that the control sample had relatively higher toughness than other samples during 14 days of storage, due to the absorption of high moisture. However, the shrimp cracker was shrunk and returned to the original small shape (No fried) at 35 day of storage, and the toughness could not be tested by the texture analyzer due to the small shape. Furthermore, the toughness of the shrimp cracker stored in coated-PLA film and PLA neat film is increased by 40.7% and 51.6% at day 7 of storage, respectively, and the toughness was increased by 50.2% and 54.7% at day 14 of storage, respectively, compared with the fresh fried shrimp cracker. It was indicated that the shrimp cracker stored in coated-PLA film has a lower increased rate than stored in PLA neat film during 14 days of storage. Because the shrimp cracker stored in PLA neat film has higher moisture content than stored in coated-PLA film during 14 days of storage, and the strength of air cell structure of shrimp cracker was more likely decreased, water could fluidize the structure of shrimp cracker, and the toughness would more increase (Luyten *et al*., 2004). However, lower toughness of shrimp cracker stored in coated-PLA film than stored in PLA neat film was observed at day 35 of storage, due to the shrinkage of the shrimp cracker, which stored in PLA neat film, was occurred and lost the moisture (Figure 29). Moreover, the shrimp cracker stored in coated-PLA film and PLA neat film were the same as the control sample and returned to the original small shape at day 56 of storage. The toughness could not be tested by the texture analyzer due to the small shape.

Thus, it was found that coated-PLA film was more effective to maintain the texture properties of shrimp cracker than PLA neat film, but the coated-PLA film still showed relatively lower water vapor barrier property compared with nylon/ LLDPE film and LDPE film.

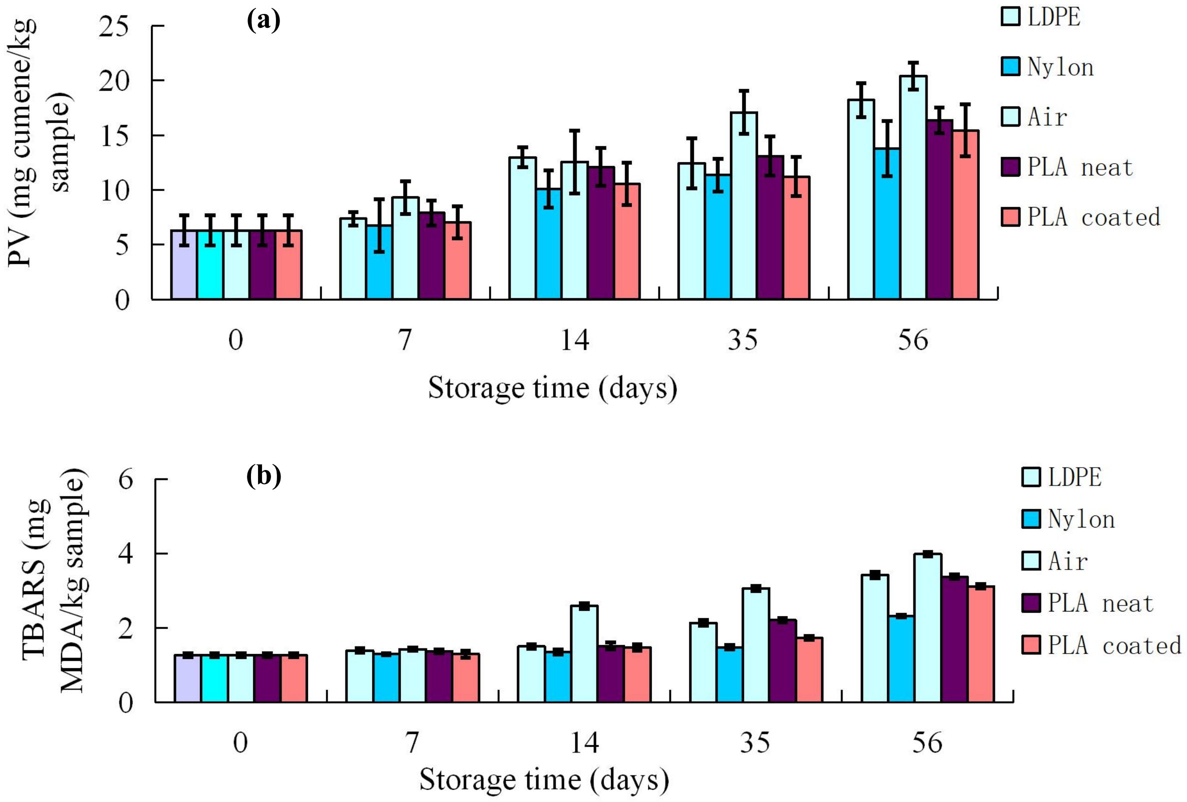

Figure 33(a) PV and (b) TBARS value of shrimp cracker stored in coated-PLA film, PLA neat film, LDPE film and nylon/ LLDPE film during 56 days of storage at 30 ± 0.5°C and 65 ± 5 % RH in comparison with the control (Fried shrimp cracker without packaging)

3.3.6.4 Determination of PV

Lipid is a very important component of food. It provides the good properties for food, such as flavor and odor. Lipid would also be degraded by the oxidation reaction. Oxidation of lipid not only produce undesirable effects, including loss of functional properties and loss of nutritional values, but the secondary products of lipid oxidation might be formed toxic compounds and colored products that cause the food poisoning (Frankel, 2014).

The peroxide value (PV) is a common method to determine the lipid peroxide, which is the primary product of lipid oxidation. Figure 33 (a) shows the PV of shrimp cracker stored in coated-PLA film, PLA neat film, LDPE film and nylon/ LLDPE film during 56 days of storage in comparison with the control (Fried shrimp cracker without packaging). It was found that all samples increased of PV-value during storage, due to the lipid oxidation (Yanishlieva and Marinova, 2001). The polyunsaturated fatty acids changes in shrimp cracker could be initiated by the free radicals and formed the lipid peroxides (Maisuthisakul *et al*., 2007). PV-value of shrimp cracker stored in nylon/ LLDPE had the lowest change compared with other samples. Because nylon/ LLDPE film had high oxygen barrier property. The control sample had the highest rate of increase in PV-value. In particular, PV-value of control sample was increased by 69.1% at day 56 of storage compared with the PV-value of fresh fried shrimp cracker. Because the control sample was exposed to the environment directly and it had the largest contact area with the air. These would promote the rate of lipid oxidation and the carbonyl compounds and hydroperoxides were formed (Noomhorm *et al*., 1997). Moreover, PV-value of shrimp cracker stored in PLA neat film is more increase than stored in coated-PLA film during 56 days of storage. Because the coated-PLA film could provide a high effective water vapor and oxygen diffusion length and the film exhibited lower WVP-value and OPC-value than PLA neat film (See in Table 14). Moreover, PV-value of the shrimp cracker stored in LDPE film and coated-PLA film is 18.2 mg cumene/kg and 15.4 mg cumene/kg, respectively, at day 56 of storage. It further confirmed that coated-PLA film had a superior oxygen barrier property than LDPE film. As a result. the shrimp cracker stored in coated-PLA film could decrease the rate of lipid oxidation and it was more effective than PLA neat film and LDPE film. Thus, coated-PLA film could be used as a food packaging material to retard the rancidity.

3.3.6.5 Determination of TBARS value

Figure 33 (b) shows the TBARS value of shrimp cracker stored in coated-PLA film, PLA neat film, LDPE film and nylon/ LLDPE film during 56 days of storage in comparison with the control (Fried shrimp cracker without packaging). Generally, the TBARS was widely used to measure the secondary by-product of lipid oxidation (Nunez- Flores *et al*., 2013), including off- flavor, compounds such as rancid of ketones, alcohols, hydrocarbons, acids, epoxides (Frankel, 2014). In Figure 33(b). TBARS values of all samples were increased during 56 days of storage. Shrimp cracker stored in nylon/ LLDPE film had lower change of TBARS value during storage compared with other samples. The control sample had the highest TBARS values. In particular, the control sample had a sharp growth of TBARS values by 51.2% compared with the fresh fried shrimp cracker at day 14 of storage, due to the highest moisture content in control sample (See in Figure 29). The rate of lipid oxidation would be promoted with high moisture content in food (Partanen *et al*., 2008). Because the water would be accelerated the movement of the prooxidants and other reactants. Prooxidants would promote the rate of lipid oxidation (Nilsuwan *et al*., 2016). Moreover, TBARS values of shrimp cracker stored in coated-PLA film had lower increase than stored in PLA neat film and LDPE film during storage. That might be ascribed to the higher oxygen barrier properties of coated PLA film (See in Table 14). This result was also agreed with PV. Thus, TBARS values of shrimp crackers would be affected that stored in different films. Coated-PLA film could retard the TBARS value more effective than PLA neat film and LDPE film, and it could be an alternative to maintain the chemical quality of shrimp cracker.

3.3.6.6 Change in color of shrimp crackers during storage

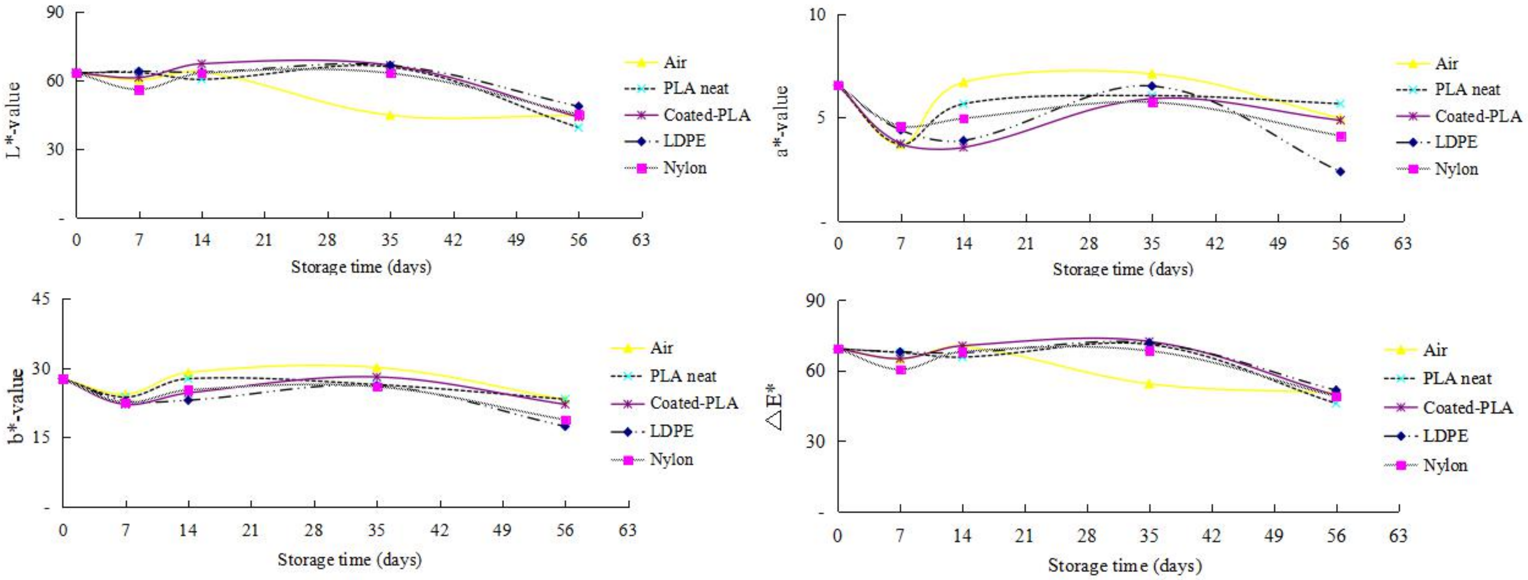

Figure 34 Color of shrimp crackers stored in coated-PLA film, PLA neat film, LDPE film and nylon/ LLDPE film during 56 days of storage at 30 ± 0.5°C and 65 ± 5 % RH in comparison with the control (Fried shrimp cracker without packaging) (L*, a*, b* and △E-values indicate lightness/ brightness, redness/ greenness, yellowness/ blueness and total color difference, respectively)

Color changes of shrimp crackers stored in coated-PLA film, PLA neat film, LDPE film and nylon/ LLDPE film in comparison with the control (Fried shrimp cracker without packaging) during 56 days of storage are depicted in Figure 34. Color parameters of control sample were totally different, as compared with others. Because the control sample was contacted with the air directly, it was easier oxidized than other samples. The a*, b*-values of control sample had a sharp growth at the first two weeks, and then the values kept stable up to 56 days. Because the control sample had a sharp growth of moisture content during two weeks of storage, lipid oxidation was accelerated and more pigments might be formed. The control sample was loss of large water after two weeks, the rate of lipid oxidation was decreased. Moreover, the control samples exhibited the lowest L*-values. Decreased L*- values indicated that the shrimp cracker became more brownness. It might be ascribed to the non-enzymatic browning reaction (Solomon *et al*., 1995). The browning was also likely associated with the lipid oxidation. Furthermore, an increasing of b*- values indicated that the yellowish substance was formed. It might be ascribed to the Maillard reaction. The increased of b*-values was related to the lipid oxidation. Moreover, the moisture content in shrimp cracker affected the Maillard reaction and lipid oxidation of food products (Artharn *et al*., 2009). The reaction was increased with the moisture content in shrimp crackers increased. The increase of lipid oxidation could also be determined by the increase of PV and TBARS values. On the other hand. Shrimp cracker stored in nylon/ LLDPE film showed the lowest rate of color changes during 56 days of storage. The lower L* -value (lightness) and higher a*-value (redness) of shrimp cracker stored in PLA film are observed than stored in coated-PLA film during 56 days of storage. The b*-value (yellowness) of shrimp cracker stored in PLA neat film is observed more increase than stored in coated-PLA film during storage. Thus, the different packaging film could affect the color of shrimp cracker. It was likely associated with the lipid oxidation taken place in the sample.

3.4 Conclusions

Shrimp cracker stored in coated PLA film could decrease the moisture content and maintained the textural properties better than PLA neat film during storage, but it still showed a lower water vapor barrier property than nylon/ LLDPE film and LDPE film. However, coated-PLA film could retard the lipid oxidation and it was more effective than PLA neat film and LDPE film. Therefore, coated- PLA film could be used as a food packaging material to retard the rancidity, but the improvement of water vapor barrier property was still needed.

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CHAPTER 4

SUMMARY AND FURTHER WORKS

4.1 Summary

PLA and silica hybrid coated films were synthesized. Oxygen and water vapor barrier properties of coated-PLA films were promoted by adding silane coupling agent ICPTES and performing UV-irradiation for 1h. Besides, SEM imagine showed that there was no phase separation on the surface and cross-section of coated-PLA film. However, the water vapor barrier property of coated-PLA film was still lower than LDPE film and nylon/ LLDPE film. Moreover, it was also found that coated-PLA film could retard the lipid oxidation for shrimp cracker which was more effective than PLA neat film and LDPE film. Therefore coated-PLA film could be an alternative to maintain the physical and chemical quality and extend the shelf-life of shrimp cracker. But the improvement of water vapor barrier property was still needed.

4.2 Further works

Coated-PLA film was effective to retard the lipid oxidation for shrimp cracker. The lower water vapor barrier property of coated-PLA film was also found. Thus, it is interesting and significant to investigate the improvement of water vapor barrier property in the further study. Meanwhile, the coated-PLA film still has a big scale for increasing other properties comparing with nylon/ LLDPE film, such as the oxygen barrier property.

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