



ENHANCEMENT OF MECHANICAL PROPERTIES AND STABILITY  
OF SHELLAC BY FORMATION OF COMPOSITE POLYMER WITH GELATIN

By

Sitthiphong Soradech

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE

Program of Pharmaceutical Sciences

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การเพิ่มสมบัติเชิงกลและความคงตัวของเซลลูล์กโดยการเตรียมในรูปคอมโพสิต  
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The Graduate School, Silpakorn University has approved and accredited the thesis title of “Enhancement of Mechanical Properties and Stability of Shellac by Formation of Composite Polymer with Gelatin” submitted by Mr. Sitthiphong Soradech as a partial fulfillment of the requirements for the degree of Master of Science in Pharmaceutical Sciences.

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The purpose of this study was to enhance the mechanical properties and stability of shellac by the formation of composite polymer with gelatin. The study of composite polymers based on shellac and various concentrations of gelatin was prepared in free film by casting method and also investigated for physicochemical properties such as acid value, insoluble solid, chemical structure, thermal analysis, powder X-ray diffraction, morphology, wettability, surface free energy, water content, water solubility, water uptake, moisture sorption isotherm, water vapor permeability and mechanical properties. The results demonstrated that the modification of shellac by the formation of composite polymer with gelatin could improve the strength and flexibility of shellac as the gelatin increased to 50%. Further study was to investigate the effect of gelatin content on stability of shellac. The stability studies of all film samples were performed at 40 °C and 75% RH in the stability chamber and investigated for the change in physicochemical properties upon storage for 180 days. The result showed that the modification of shellac by formation of composite polymer with gelatin at the high concentrations (30, 40 and 50%) could protect among carboxyl and hydroxyl groups of shellac, resulting in the increase in stability of shellac under the long period of storage for 180 days. However, the composite polymer with gelatin could not prolong the brittleness and fracture of shellac under the long period of storage. Therefore, the addition of plasticizer played an important role for improving the mechanical properties of composite polymer. Among concentrations of gelatin, 40% gelatin was the suitable concentration for further study. Two types of plasticizers i.e., polyethylene glycol 400 (PEG 400) and diethyl phthalate (DEP) at 5 and 10% w/w were chosen to study. The addition of both types and concentrations of plasticizers could improve the stability of composite polymer in term of mechanical properties upon 180 days of storage. Between both plasticizers, PEG 400 at 5% was the proper type and concentration for further investigation. The film coating efficiency of shellac over hydrophilic and hydrophobic substrates was then evaluated. The coating potential of shellac over hydrophilic substrate could be modified by the addition of gelatin and hydrophilic plasticizer while the hydrophobic surface and addition of hydrophobic plasticizer in the composite polymer showed the opposite trend. Further investigation was to study the application of composite polymer based on 40% gelatin unplasticized and plasticized with 5% PEG 400 as film coating for extending the shelf life of banana under the longer period. The result indicated that the composite polymer could prolong the aging of banana for more than 30 days in comparison to uncoated banana indicated by the slower change in color, sugar, acid, weight loss and firmness. Hence, the disadvantages of shellac could be improved by the modification of shellac into the formation of composite polymer and addition of plasticizer, contributing to the wide application of film coating in food and pharmaceutical industries.

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Program of Pharmaceutical Sciences Graduate School, Silpakorn University Academic year 2010

Student's signature .....

Thesis Advisor's signature .....



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## CHAPTER 1

### INTRODUCTION

#### **1. Statement and significance of the research problem**

Shellac has been widely studied for applying as an edible film coating which is a special natural polymer, obtained from purified resinous secretion of lac insects, *Laccifer Lacca*. It mostly cultivates on host trees from India and Thailand (Krause and Müller 2001 : 89-92; Yu et al. 2006 : 576-602). It is composed of hard resin and soft resin of polyesters and single esters that containing hydroxyl and carboxyl groups (Upadhye et al. 1970 : 4177-4187; Singh et al. 1974 : 867-874; Singh et al. 1974 : 3689-3693). It is an excellent film forming, good barrier properties, soluble in alcohol and alkaline solution (Sontaya Limmatvapirat et al. 2004 : 41-49; Manee Luangtana-anan et al. 2007: 687-692; Sontaya Limmatvapirat et al. 2007: 690-698). Therefoere, the shellac has been widely used in food industries and agro industries for water, gas, lipid and microbial spoilage protection and hence prolonging the shelf-life of products (Hagenmaier and Baker 1993 : 283-287; McGuire and Hagenmaier 1996 : 100-106; Valencia-Chamorro et al. 2009 : 72-79) and has been used for moisture protection of drugs, controlling the delivery and enteric coating of drug and probiotic (Pearnchob et al. 2004 : 313-321; Sontaya Limmatvapirat et al. 2004 : 41-49; Stummer et al. 2010 : 1312-1320).

However, there are many drawbacks in limiting usage of shellac such as batch-to-batch variation, poor mechanical property and instability, resulting in less use of shellac in comparison to synthetic polymer (Luce 1978 : 51-55; Manee Luangtana-anan et al. 2007 : 687-692; Sontaya Limmatvapirat et al. 2007 : 690-698; Manee Luangtana-anan et al. 2010 : 12934-12940). Generally, edible films obtained from shellac show the poor mechanical strength and brittleness. The puncture strength of native shellac film was 1.0-2.0 MPa and the percent elongation of native shellac film was 1.0-3.0 %, lower than other natural polymers (Pearnchob et al. 2004 : 313-321; Sontaya Limmatvapirat et al. 2007 : 690-698).

There are several reports improving the mechanical property of shellac by many methods such as the incorporation of plasticizers, the modification of shellac in salt form and hydrolyzed shellac. However, the improvement could be seen only for the brittleness of shellac films, not the mechanical strength of shellac (Sontaya Limmatvapirat et al. 2004 : 41-49; Manee Luangtana-anan et al. 2007 : 687-692; Sontaya Limmatvapirat et al. 2007 : 690-698). In addition, the aging and the degradation are the long existence of problem due to the polymerization among hydroxyl groups and carboxyl groups, causing the instability of shellac (Luce 1978 : 51-55; Specht 1998 : 20-28). Luce reported that tablets coated with shellac could not disintegrate upon storage for only 1 year as a result of the polymerization (Luce 1978 : 51-55). Few approaches have been attempted to improve the physicochemical properties and stability of shellac such as addition of plasticizers, modification of shellac in salt form and derivatives (Pearnchob et al. 2004 : 313-321; Sontaya Limmatvapirat et al. 2005 : 47; Manee Luangtana-anan et al. 2007 : 687; Sontaya Limmatvapirat et al. 2007 : 690-698 ; Sontaya Limmatvapirat et al. 2008 : 335-344; Manee Luangtana-anan et al. 2010 : 12934-12940). From previous study, the instability of shellac could improve when shellac prepared in ammonium salt form. It is a result of the protection of ammonium at the carboxylic groups of shellac, attributing to less polymerization. However, the modification of shellac in ammonium salt form could protect the instability of shellac only 90 days of storage, due to the loss of ammonium ion when storage at 75% RH, 40 °C (Manee Luangtana-anan et al. 2007 : 687-692; Sontaya Limmatvapirat et al. 2007 : 690-698).

Composite polymer is an effective method for providing a new material in particular for various applications. The composite polymer could be produced by blending two or more different polymers which can be expected to have better mechanical properties and barrier properties and stability of polymer (García et al. 2004: 339-345). Various combinations of two natural polymers are proteins and polysaccharides, proteins and lipids, polysaccharides and lipids, and synthetic polymers and natural polymers (Yu et al. 2006 : 576-602; Bourtoom. 2008 : 237-248). It was reported that the addition of hydrophilic polymer such as HPMC, MC and carbomer could enhance the mechanical and physical properties of shellac film. The

percentage of elongation and drug permeability through shellac film increased with an increasing of concentration of HPMC, MC and carbomer while the modulus and glass transition temperature decreased (Qussi and Suess 2006 : 403-412).

Gelatin, a natural hydrocolloid polymer, obtained from hydrolysis of collagen from skin, bones and connective tissue (Li et al. 2006 : 544-549; Gámez-Guillín et al. 2009 : 3-16) . The structure of gelatin is mostly contained with carboxyl groups and amino group on the backbone chains and has the potential to blend with other polymers, due to its ability to form the interaction (Xiao et al. 2001 : 1596-1602; Cheng et al. 2006 : 62; Dong et al. 2006 : 37-44; Farris et al. 2011 : 61-70). Moreover, gelatin is a biodegradable polymer with many attractive properties such as abundance of raw material, biodegradability, excellent film forming, biocompatibility, plasticity, adhesiveness and good mechanical properties. It has been widely used in food, agro, biomedical and pharmaceutical industries (Vanin et al. 2005 : 899-907; Gámez-Guillín et al. 2009 : 3-16). Many researches have widely utilized gelatin as a secondary polymer in composite polymer formation such as protein/gelatin, alginate/gelatin, gellan/gelatin, chitosan/gelatin, glucomannan/gelatin and pectin-gelatin to improve some properties of edible film (Xiao et al. 2001 : 1596-1602; Cheng et al. 2003 : 2871-2880; Lee et al. 2004 : 251-254; Dong et al. 2006 : 37-44; Cao et al. 2007 : 1153-1162; Farris et al. 2011 : 61-70).

Therefore, the objective of this research was to investigate the approach for enhancement of the mechanical properties and stability of shellac by the formation of composite polymer with gelatin. The stability of composite polymer was then evaluated at 40 °C, 75% RH for 180 days. The appropriate ratio of composite polymer was used to further study the effect of types and concentrations of plasticizers on the mechanical properties and stability of composite polymer. The composite polymers with and without plasticizers were further tested for the coating efficiency over various substrates and to evaluate the effect of composite polymer with and without plasticizer as edible film coating on the post harvest quality and prolonged shelf life of food product during storage.

## **2. Objective of this research**

2.1 To study the formation of composite polymer based on shellac and various concentrations of gelatin for the enhancement of mechanical properties and stability of shellac

2.2 To evaluate the influence of types and concentrations of plasticizers on the mechanical properties and stability of composite polymer based on shellac and gelatin

2.3 To investigate the film coating efficiency of composite polymer and the influence of plasticizers for the coating efficiency in pharmaceutical and food applications

2.4 To apply composite polymer as edible film coating for post harvest quality and to prolong shelf life of food product

## **3. Hypothesis of this research**

3.1 The poor mechanical properties and the instability of shellac can be improved by the formation of composite polymer with gelatin.

3.2 The types and concentrations of plasticizers have an influence on the mechanical properties and stability of composite polymer based on shellac and gelatin.

3.3 The concentrations of gelatin and types of plasticizers are attributed to the change in the coating efficiency of shellac over wide range of substrates.

3.4 The application of shellac and gelatin composite polymer with and without plasticizer as edible film coating can enhance the quality and prolonged the shelf life of banana.

## **CHAPTER 2**

### **LITERATURE REVIEWS**

#### **1. Introduction to edible film and coating**

Edible film and coating have long been attracted much attention in food and pharmaceutical industries, because it could partly substitute for the traditional non-biodegradable synthetic films, inexpensive, produces from renewable resources, edibility, biocompatibility, biodegradability, barrier properties and non-pollution, which could be prepared from natural polymer such as proteins, polysaccharides, lipids and special natural polymer (Chen 1995 : 2563-2583; Flores et al. 2007 : 257-265; Chillo et al. 2008 : 159-168).

(1) Polysaccharides are widely used in edible films and coatings, e.g. cellulose, starch derivatives, pectin derivatives, seaweed extracts, exudates gums, microbial fermentation gums and chitosan which are generally very hydrophilic polymer, attributing to the poor water vapor and gas barrier properties. However, the film coating by polysaccharide polymers may not provide a good water vapor barrier which can act as sacrificing agents retarding moisture loss from food products (García et al. 2004 : 339-345; Bourtoom 2008 : 237-248; Chillo et al. 2008 : 159-168; Famí et al. 2011: 1226-1231; Farris et al. 2011 : 61-70; Saxena et al. 2011 : 619-623).

(2) Lipid compounds are usually used for a protective coating of food and pharmaceutical product that contain acetylated monoglycerides, natural wax, and surfactants. The most effective lipid substances are paraffin wax and beeswax. The function of a lipid coating is to protect transport of moisture, due to the low polarity. However, the hydrophobic characteristics of lipid give the high thicker and low mechanical property of lipid films, resulting in the more brittleness of film. Generally, the decrease in water vapor permeability of film is obtained when the concentrations of hydrophobic polymer increases. Lipid-based films are supported on a polymer structure matrix, usually a polysaccharide, to provide mechanical strength (Yang and Paulson 2000 : 571-578; Bertan et al. 2005 : 73-82; Bourtoom 2008 : 237-248; Wang et al. 2009 : 11-19).

(3) Protein is a water insoluble polymer which obtains from animal tissues or globular proteins. It is soluble in water or aqueous solutions of acids, bases or salts and functions widely in living systems. It is typically divided into fibrous and globular proteins. Fibrous proteins are extended and related closely with each other in structures, generally by hydrogen bonding, to form fibers. The globular proteins fold into complicated spherical structures held together by a combination of hydrogen, ionic, hydrophobic and covalent bonds. The chemical and physical properties of these proteins depend on the relative amounts of the component of amino acid residues and their placement along the protein polymer chain (Chambi and Grosso 2006 : 458-466; Bourtoom. 2008 : 237-248; Chiou et al. 2008 : 3748-3753; Cao et al. 2009 : 729-735; Gámez-Guillín et al. 2009 : 3-16; Su et al. 2010 : 145-153; Martucci and Ruseckaite 2011 : 377-383).

(4) Special natural polymer is another polymer which could be classified in three groups, due to the different chemical structures of polymers including shellac, lignin and rubber. It is widely used in edible film and coating, polymer science and chemical engineering (Yu et al. 2006 : 576-602; Bourtoom 2008 : 237-248).

## **2. Background of shellac**

Shellac has been widely studied for applying as edible film coating which is a special natural polymer from purified resin derived from lac insects, *Laccifer Lacca* which parasitically grows on some specific types of trees in China, India, and Thailand (Krause and Müller 2001 : 89-92; Yu et al. 2006 : 576-602) which can be found on *Samanea Saman* and *Leucaena Leucocephala* trees, family of *Leguminosae* (Manee Luangtana-anan et al. 2007 : 687-692). Thailand is the second large exporter of lac as a raw material of shellac in the world.



Figure 1 Physical characteristic of shellac

Source : Furniture restoration products, Shellac [Online], accessed 8 May 2010. Available from <http://www.furniture restoration.co.nz/products/shellac.php>

### **2.1 Chemical structure of shellac**

The chemical structure of shellac is composed of polyhydroxy carboxylic acids that contain aleuritic acid (9, 10, 16-trihydroxy palmitic acid), butolic acid (6-hypalmitic acid), butolic acid (6-hydroxy tetradecanoic acid), tetradecanoic acid and alicyclic sesquiterpenic compounds (Sarkar and Shrivastava 1997 : 370-377). Generally, shellac is mostly consisted of 70% hard resin and 30% soft resin of polyesters and single esters that containing several hydroxyl groups and carboxyl groups (Upadhye et al. 1970 : 4177-4187; Singh et al. 1974 : 867-874; Singh et al. 1974 : 3689-3693; Sontaya Limmatvapirat et al. 2008 : 335-344) as shown in Figure 2. In addition, the component of shellac is denpendent on the season of cultivation and type of tree in cultivating lac insect, etc.

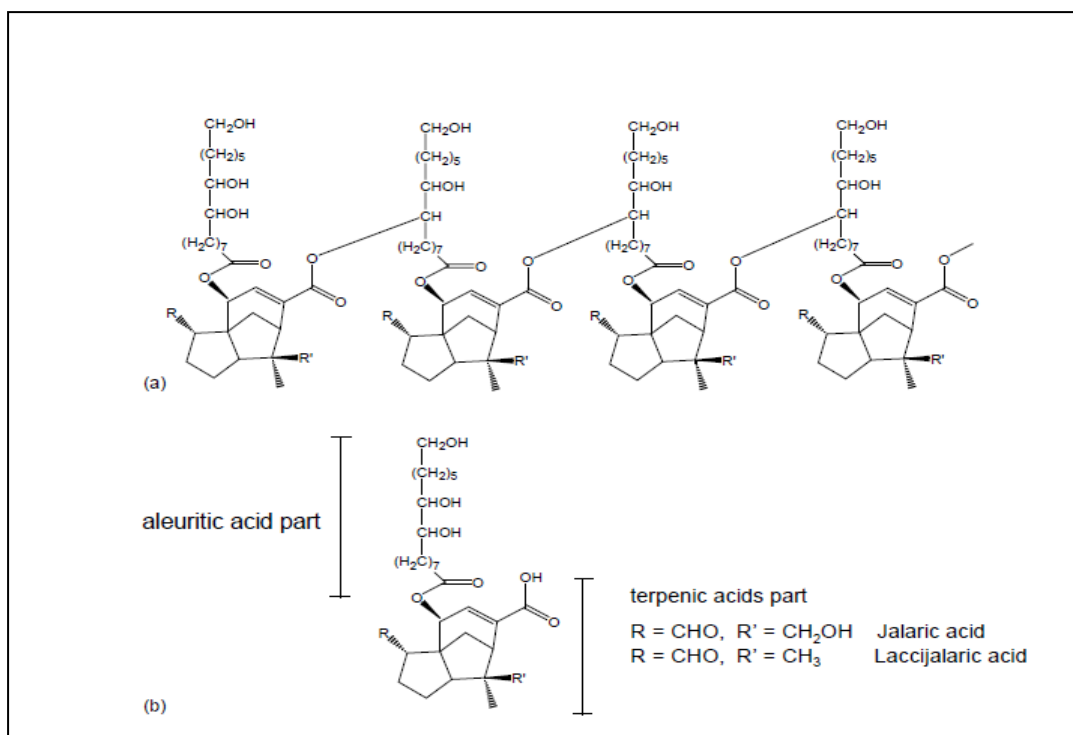


Figure 2 Chemical structure of shellac

Source : Sontaya Limmatvapirat et al., "Modification of physicochemical and mechanical properties of shellac by partial hydrolysis," International Journal of Pharmaceutics 278 (2004) : 42.

The chemical structure of shellac could be detected by FTIR spectroscopy as shown in Figure 3a. The FTIR spectrum of shellac shows the characteristic peaks at  $3,438\text{cm}^{-1}$  due to the intermolecular H-bonding of hydroxyls at  $2,925$  and  $2,853\text{cm}^{-1}$  attributed to C-H stretching of aliphatic  $-\text{CH}_2-$  and  $-\text{CH}_3$  and at  $1,718\text{cm}^{-1}$  due to C=O stretching of  $-\text{COOH}$  overlapping with C=O stretching of  $\alpha, \beta$ -unsaturated ester. The ethenoid C=C stretch appears at  $1,636\text{cm}^{-1}$  as a shoulder of the stronger C=O peak. Asymmetric bending and deformation modes of  $-\text{CH}_2-$  and  $-\text{CH}_3$ , as well as symmetric deformations of C- $\text{CH}_3$ , appear as unresolved peaks at  $1,454$  and  $1,375\text{cm}^{-1}$  respectively. The absorption bands at  $1,252$  and  $1,158\text{cm}^{-1}$  represent the O-H bending and C-O stretching of aliphatic carboxyl and hydroxyl groups overlapping with C-O stretch of  $-\text{COOR}$ . The C-O stretching of ether/acetal linkage attributed to the unresolved band at  $1,032\text{cm}^{-1}$ . The absorption band at  $937\text{cm}^{-1}$  may be attributed to the rocking vibration of the C- $\text{CH}_3$  superimposed with

C-H wag of the disubstituted *trans* olefin. C-H bending (out of plane) of *cis* alkene appears as a sharp peak at  $721\text{cm}^{-1}$  (Sarkar and Shrivastava 1997 : 370-377).

### 2.2.1 Chemical structure of hard resin

The insoluble portion of the lac resin constitutes nearly 70 percent of the total resin and is chiefly responsible for the characteristic resinous properties of lac. The FTIR spectrum of hard resin (Figure 3b) indicates the absorption band of  $n\text{CH}=\text{CH}$ . The  $d\text{CH}=\text{CH}$ , which is also diminished as comparison to parent shellac. However, the hard resin is composed of chemical structure with the same shellac (Sarkar and Shrivastava 1997 : 370-377).

### 2.2.2 Chemical structure of soft resin

This soluble portion of lac (30 per cent) shows a broad peak at  $3,392\text{ cm}^{-1}$  representing the H-bonding of hydroxyl groups as shown in Figure 3c. The FTIR spectrum of soft resin indicates the absorptions band at  $941$  and  $721\text{cm}^{-1}$ , due to  $\text{C}=\text{C}-\text{H}$  bending vibrations of *trans* and *cis* substituted olefins respectively. Since soft resin has an iodine value of 50-55, the above spectral features unequivocally confirm that soft resin has a higher hydroxylic and unsaturated content in comparison with hard resin. This can be explained as being due to the presence of 16-hydroxy-*cis*-9-hexadecenoic acid and 6-hydroxy-tetradecanoic acid (butolic acid) in soft resin but absent in hard resin (Sarkar and Shrivastava 1997 : 370-377).

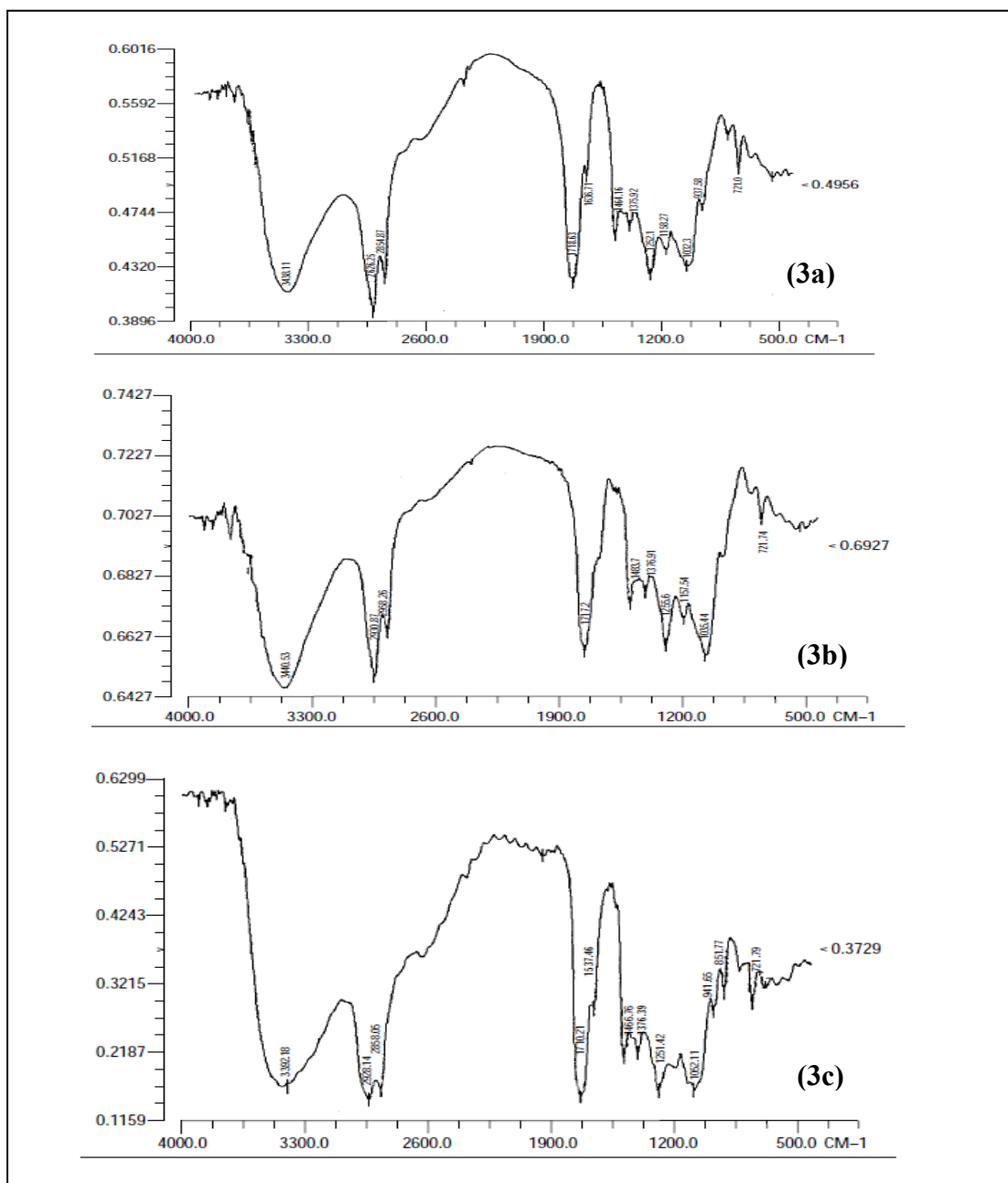


Figure 3 FTIR spectra of shellac (3a), hard resin (3b) and soft resin (3c)

Source : P.C. Sarkar and A.K. Shrivastava, "FTIR spectroscopy of lac resin and its derivatives," *Pigment and Resin Technology* 26 (1997) : 371–372.

## 2.2 Basic characteristics of lac insect

Lac is one of insect which lives on trees called lac host trees where it secretes the lac resin or sticklac. It is scrapped off and manufactured into shellac. Lac insect is distributed in Tropical Asia such as India, Pakistan, Bangladesh, Myanmar, Thai, South China, Taiwan, etc. There are about 20 species in the world. However, only two species, *Laccifer lacca* in India and China and *L. Chinensis* in China and Thailand, has been used for industrial purpose. The life cycle of a lac insect takes about six months and consists of four stages: egg, larva, pupa and adult as shown in Figure 4. In this cycle, the lac industry obtains two lac crops each year from each tree. Lac insect can be very destructive to trees, stunting or killing twigs and branches of the host trees by inserting their long suctorial mouthpart into the tree and draw out sap. Lac insects do not only drain out the sap but they also transmit germ. Therefore, we must realize lac insect is vermin for plant (Bounthanh Keoboulapha, Niphavanh Philavanh and Attachai Jintrawet 2011 : 1-10).

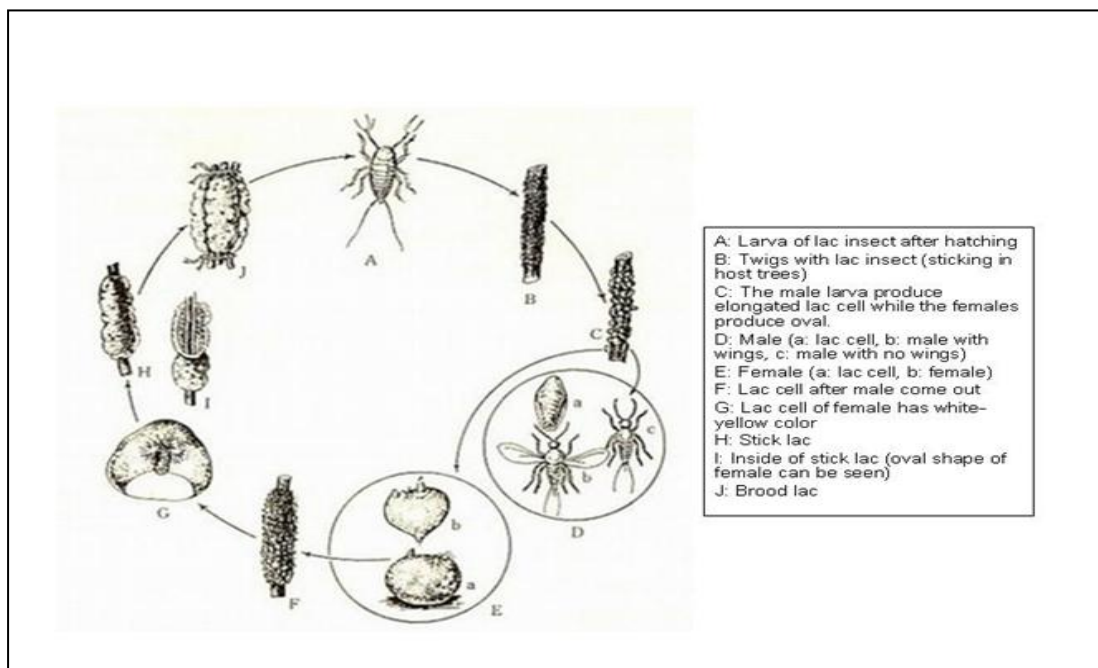


Figure 4 Lac insect life cycle (*Kerria lacca*)

Source : Bounthanh Keoboulapha, Niphavanh Philavanh and Attachai Jintrawet, Intensifying upland rice systems with stick lac production in Northern Lao PDR [Online], accessed 19 January 2011. Available from <http://www.mcc.cmu.ac.th>

### **2.3 Host trees for lac insect**

Pigeon pea has been promoted by researches and extension agencies, and projects for improving fallows, hedgerows, cropping systems: rotation, intercropping, alley cropping etc. This is negligible by farmers, although pigeon pea is proved to be good crop for soil improvement, weed suppression, and reducing nematode in upland rice. In Huay lek village, Ngoi district, Louang Prabang province, although there are at least 10 host species listed by the villagers, only few species are currently used for stick lac production. Pigeon pea has been planted as a lac host tree in the village since 2003 and now it can be seen in many surrounding villages. Recently, Mai Liang „Liang tree“ is integrated to pigeon pea for stick lac production by many villagers in Luang Prabang (Bounthanh Keoboulapha, Niphavanh Philavanh and Attachai Jintrawet 2011 : 1-10).

### **2.4 Products obtained from lac insect**

Lac is considered as natural gift to mankind which is the only known commercial resin of animal origin. Generally, the products obtained from lac insect can be divided into four categories, including, sticklac (the raw material), seedlac (the semi processed), shellac (finished product) and bleached shellac (the improvement of color of shellac). The characteristics of product obtained from lac insect are shown in Figure 5.

(1) Sticklac is a raw material which is first crushed and sieved to remove certain impurities. It is then washed in large vats or barriers to remove insect bodies and a portion of the coloring matter. Washing is repeated until the dye and most of the impurities are removed. The cleaned stick lac thus is spread on large clean open air floor to dry. The composition of sticklac contains of resin (70-80%), wax (6-7%), lac dye (4-8%), impurity (15-25%), moisture (3.5%) and other components (12.5%).

(2) Seedlac is semi process of shellac which removes the sticks and stones etc. As far as possible by crushing, sieving and winnowing, and washing out the dye with water yields the semi-refined product known as seedlac, from its general appearance, in the form of grain of 10 mesh or smaller, and yellow or reddish brown in color. It depends on the host tree and the district from which the sticklac has been

collected. Adhering impurities on these grains of seedlac amount to 3-8 percent, averaging 5%.

(3) Shellac is the end product produced by removal of wax and other impurities from the seedlac by heat seedlac until it melts and can ship in dry or flaked form and is re-moisturized with an alcohol solvent, generally denatured alcohol.

(4) Bleached shellac is prepared by dissolving in sodium carbonate and centrifuge to remove insoluble and then bleached with sodium hypochlorite (Manee Luangtana-anan and Tanasait Ngawhirunpat 2003 : 153-165; Bounthanh, Niphavanh and Attachai 2011 : 1-10).

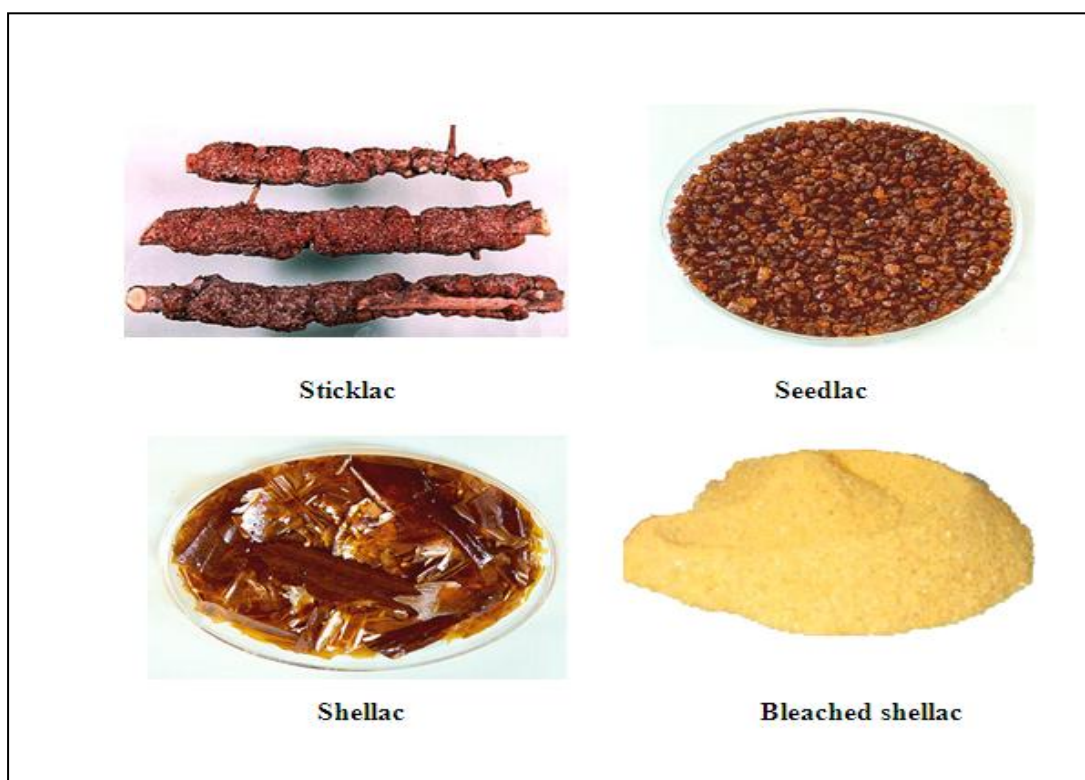


Figure 5 Products obtained from lac insect

Source : Manee Luangtana-anan and Tanasait Ngawhirunpat, ed. Application of Polymer Technology for the Development of Pharmaceutical, Coasmetic and Health Products, Nakorn prathom : Silpakorn Univerity, 2003 : 155.

## 2.5 Classification of shellac

Generally, the shellac can be classified in four groups including; orange shellac, dewaxed orange shellac, bleached shellac and refined wax-free bleached shellac. The characteristic and production process of different shellac were shown as follows:

(1) Orange shellac is a refined lac, which is soluble in alcohol that contains some wax and resin.

(2) Dewaxed orange shellac is produced either by a process of filtration in the molten state or by hot solvent process or both which dewaxed and may contain lesser amounts of the natural color than original shellac.

(3) Bleached shellac is prepared by dissolving the Lac in aqueous sodium carbonate, bleaching the solution with sodium hypochlorite and precipitating the bleached shellac with 2N sulfuric acid, giving the white color of shellac.

(4) Refined wax-free bleached shellac is obtained after bleached shellac process and then removing the wax by filtration, during the process results in refined bleached shellac (Manee Luangtana-anan and Tanasait Ngawhirunpat 2003 : 153-165).

## 2.6 Properties of shellac

Generally, shellac is reported to have some good properties, which is attributed to widely use of shellac in various industries.

(1) Excellent film forming, shellac is chemically similar to synthetic polymers, and hence can be considered a natural form of plastic. It can be turned into a moulding compound when mix with wood flour and mould under heat and pressure methods, so it can also be classified as thermoplastic.

(2) Soluble in alcohol and alkaline solution, shellac is soluble in alkaline solutions such as ammonia, sodium borate, sodium carbonate, and sodium hydroxide, and also in various organic solvents. When shellac is dissolved in mixture of ethanol and methanol, it yields a coating of superior durability and hardness.

(3) Low water vapor permeability, the water vapor permeability coefficient of shellac is still in a low level as compared to the reported values ( $1 \times 10^{-7}$  to  $3 \times 10^{-5} \text{ g h}^{-1} \text{ m}^{-1} \text{ Pa}^{-1}$ ) of several synthetic polymers, i.e., cellulose acetate phthalate (CAP), hydroxypropyl methylcellulose phthalate (HPMCP, HP-55), hydroxypropyl

methylcellulose acetate succinate (HPMCAS, ASLG) and methacrylic acid-ethyl acrylate copolymer (Eudragit L30D), attributed to the higher protection of shellac to moisture and water and result in the higher quality of product and prolonging the shelf life of product.

(4) Low acid permeability, shellac is insoluble in acid attributed to a good resistance in gastric fluids which could be utilized shellac in enteric coating applications i.e., sealing enteric coating and controlled drug release.

(5) Good adhesive, shellac film shows excellent adhesion to a wide variety of surfaces, possessing high gloss, hardness and strength.

(6) Low conductivity, shellac is powerful bonding material with low thermal conductivity and a small coefficient of expansion. The thermal plasticity and capacity of absorbing large amounts of filters are found (Luce 1978 : 51-55;; Krause and Müller 2001 : 89-92; Manee Luangtana-anan and Tanasait Ngawhirunpat 2003 : 153-165; Sontaya Limmatvapirat et al. 2004: 41-49; Qussi and Suess 2005 : 99-108; Accaseavorn et al. 2006 : 42-45; Qussi and Suess 2006 : 403-412; Manee Luangtana-anan et al. 2007 : 687-692; Sontaya Limmatvapirat et al. 2007 : 690-698; Manee Luangtana-anan et al. 2010: 12934-12940; Stummer et al. 2010 : 1312-1320).

## **2.7 Applications of shellac**

The good properties of shellac lead to the wide utilization of shellac in various applications. In pharmaceutical industry, it has been used for moisture protection of drugs, controlled delivery and enteric coating for drug and probiotic (Pearnchob et al. 2004 : 313-321; Sontaya Limmatvapirat et al. 2004 : 41-49; Stummer et al. 2010 : 1312-1320). In food industry, it has been extensively used for oxygen, water, gas, lipid and microbial spoilage protection and also extending the shelf-life of product (Walker and Steele 1923 : 707-708; Hagenmaier and Baker 1993 : 283-287; McGuire and Hagenmaier 1996 : 100-106; Accaseavorn et al. 2006 : 42-45; Chauhan et al. 2011 : 961-966). In printing industry, it has been use in flexographic ink, waterproof ink, photo engraving. In textiles industry, it has been widely used in stiffening of hats. In cosmetic industry, it is widely utilized in hair lacquer, coating for enteric pills and dental base place. In electrical industry, it has been used in micanite, insulating varnish. In photography application, shellac is widely used for dry mounting tissue paper, protective varnish. In paper industry, it is

used in paper varnish and playing cards. In rubber industry, it is used for stiffening agent and surface finishing. In adhesive field, it is widely utilized in Gasket cement, sealing wax and pyrotechnic optical cement (Walker and Steele 1923 : 707-708; Bourtoom 2008 : 237-248).

## **2.8 Drawback of shellac**

However, there are many drawbacks of shellac leading to the limited use such as batch-to-batch variation, poor mechanical property, low solubility and instability, resulting in the lesser use of shellac than other polymers (Luce 1978 : 51-55; Manee Luangtana-anan et al. 2007 : 687-692; Sontaya Limmatvapirat et al. 2007 : 690-698; Manee Luangtana-anan et al. 2010 : 12934-12940).

### **2.8.1 Variation in batch**

Upon mild hydrolysis shellac gives a complex mix of aliphatic and alicyclic hydroxy acids and their polymers varied in exact composition depending on the source of the shellac and the season of collection. The major component of the aliphatic component is aleuritic acid, whereas the main alicyclic component is shellolic acid (Manee Luangtana-anan and Tanasait Ngawhirunpat 2003 : 153-165).

### **2.8.2 Low stability**

The aging of shellac is found, because of the polymerization among hydroxyl groups and carboxyl groups, causing in the instability of shellac (Specht 1998 : 20-28; Manee Luangtana-anan et al. 2007 : 687-692). Luce reported that tablets coated with shellac could not disintegrate upon storage for only 1 year, resulting from the instability as it might be the result of the polymerization (Luce 1978 : 51-55). The instability of shellac resulted from the various factors i.e., high temperature, radiation and long storage times.

### **2.8.3 Low solubility**

Shellac molecules consist of hydroxyl and carboxyl groups. The low number of carboxylic acid per shellac molecule and the high pKa of carboxylic acid lead to the low solubility. In addition, the longer storage, the lower solubility of shellac is observed which result from the instability among these groups from esterification, indicated by the reduction of acid value and the increase in insoluble solid (Sontaya Limmatvapirat et al. 2004 : 41-49; Sontaya Limmatvapirat et al. 2008 : 335-344).

### **2.8.4 Poor mechanical properties and brittleness**

Edible films obtained from shellac generally show the poor mechanical strength and brittleness. The puncture strength of native shellac film was 1.0-2.0 MPa and the percentage of elongation of native shellac film was 1.0-3.0 %, lower than other natural polymers (Pearnchob et al. 2004 : 313-321; Sontaya Limmatvapirat et al. 2007 : 690-698; Narumol Meenabun et al. 2010 : 467-470). There are several reports improving the mechanical properties of shellac by many methods such as the incorporation of plasticizers, the formation of salt form and the hydrolysis reaction of shellac. However, the improvement could be seen only for the brittleness of shellac films, not the mechanical strength of shellac (Manee Luangtana-anan and Tanasait Ngawhirunpat 2003 : 153-165; Manee Luangtana-anan et al. 2007 : 687-692; Sontaya Limmatvapirat et al. 2007 : 690-698).

### **3. Several methods for improving the drawback of shellac**

Several approaches have been attempted to improve the physicochemical properties and stability of shellac including; partial hydrolysis (Sontaya Limmatvapirat et al. 2004: 41-49), addition of plasticizers (Qussi and Suess 2006 : 403-412; Manee Luangtana-anan et al. 2007 : 687-692; Manee Luangtana-anan et al. 2010: 12934-12940), modification of polymer in salt form (Sontaya Limmatvapirat et al. 2007 : 690-698) and derivative (Sontaya Limmatvapirat et al. 2008 : 335-344; Danuch Panchapornpon et al. 2011: 1241-1244) and preparation in composite polymer formation (Qussi and Suess 2006 : 403-412; Stummer et al. 2010 : 1312-1320).

#### **3.1 Partial hydrolysis**

The mechanical properties and solubility of shellac are the drawback of native shellac in enteric film coating. Limmatvapirat et al. attempted to improve the mechanical properties and solubility of shellac by partial hydrolysis with alkaline treatment. They found that the higher prolongation of hydrolysis contributed to the higher acid value (AV), resulting in the higher solubility of shellac in buffer solution. In addition, the films prepared from hydrolyzed shellac were more flexible and softer than those prepared from native shellac. The enhancement of flexibility was related with the increase in soft resin of shellac (Sontaya Limmatvapirat et al. 2004 : 41-49).

### 3.2 Addition of plasticizers

Plasticizer addition is one of the effective methods for providing a new material for a variety of applications. They are generally essential to overcome the brittleness of the biopolymer films. Brittleness is an inherent quality attributed to the complex/branched primary structure and weak intermolecular forces of natural polymers. Plasticizers can reduce the intermolecular forces, soften the rigidity of the film structure and increase in the mobility of the biopolymer chains, hence improving the mechanical properties (Srinivasa et al. 2007 : 1113-1122; Chen and Lai 2008 : 1584-1595; Cao et al. 2009 : 729-735). The mechanism of plasticizers within the polymer network is shown in Figure 6. It exhibits the plasticizing effect of biopolymer film (Su et al. 2010 : 145-153).

Generally, the plasticizers can be classified in two groups including hydrophilic plasticizer such as polyethylene glycol, glycerol, sorbitol, ethylene glycol etc (Yang and Paulson 2000 : 563-570; Cao et al. 2009 : 729-735) and hydrophobic plasticizer such as diethyl phthalate, dibutyl phthalate, tributyl citrate, acetyltriethyl citrate etc (Andreuccetti et al. 2009 : 1113-1121). The hydrophilic plasticizer has an influence on the increase in hydrophilic of biopolymer film leading to the increase in the water vapor permeability, water solubility, water uptake, moisture sorption isotherm and water content of biopolymer films.

There are some published studies in the literature reporting the effects of factors of plasticizers including types, molecular weight and concentration on the physicochemical properties and stability of polymer film. Many researches have been reported the types of plasticizers affected the change in physicochemical properties of film. Polyethylene glycol (PEG) which is a non-ionic water soluble polymer consisting polar ethylene glycol units have been used in methylcellulose-based films (Turhan et al. 2001 : 59-62; Manee Luangtana-anan et al. 2010 : 12934-12940). Glycerol was shown to improve the flexibility of film, reduce film puncture strength, elasticity and water vapor barrier properties of wheat gluten films (Gontard et al. 1994: 39-50). The addition of glycerol with the same concentration directly affected the enhancement of flexibility of gelatin film because glycerol could reduce the intermolecular force of gelatin molecule and exhibit the increase in elongation of film (Vanin et al. 2005 : 899-907). Poly-(methacrylic acid, methylmethacrylate 1:1,

Eudragit L) films containing various plasticizers showed strong correlation between thermal properties and mechanical properties (Gutierrez-Rocca and McGinity 1994 : 293-301). Water vapor permeability of film was changed by the addition of plasticizer. Polyethylene glycol increased water vapor permeability of hydroxypropyl methylcellulose (HPMC) film whereas castor oil and dibutyl phthalate reduced water vapor permeability. In some cases, water vapor permeability did not change by the addition of plasticizers (Saettone et al. 1995 : 83-88).

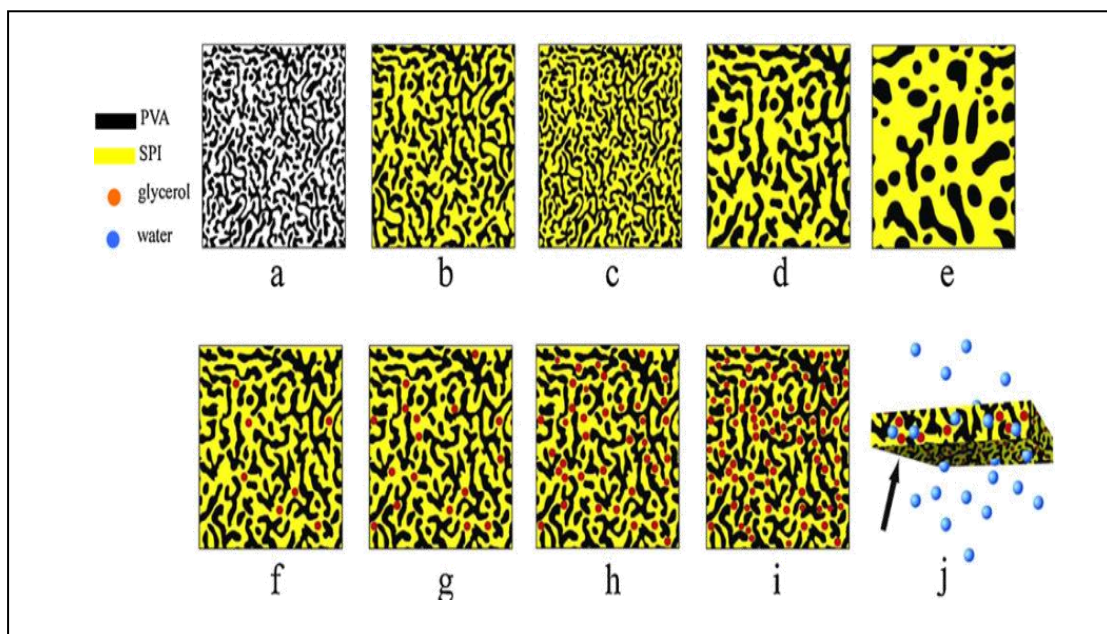


Figure 6 Proposed diagram of plasticizers interaction into polymer chain

Source : J. F. Su et al., "Moisture sorption and water vapor permeability of soy protein isolate/poly(vinyl alcohol)/glycerol blend films," Industrial Crops and Products 31 (2010) : 273.

This could be the result of the solubility and the affinity of plasticizer to the polymer. The release mechanism of theophylline coated products was also affected by the addition of plasticizer (Frohoff-Hólsmann et al. 1999 : 67-75). The stability of polymer film was dependent on the types of plasticizers. The various plasticizers such as diethyl phthalate (DEP), triacetin (TA) and polyethylene glycol 400 (PEG 400) with the same concentration had an influence on the stability of shellac films. The stability of shellac film could be predicted by the insoluble solid

parameter as shown in Figure 7. The result indicated that the percentage of insoluble solid of unplasticized shellac film extremely increased as the prolongation of storage time which confirmed the instability of shellac, due to the polymerization. The among hydroxyl groups and carboxyl groups significant change in insoluble solid was found for plasticized shellac with DEP and TA whereas the addition of PEG 400 gave the highest stability. In addition, PEG 400 might still be retained in shellac as compared to other plasticizers because of the higher molecular weight and less volatilization. The use of PEG 400 as plasticizer significantly improved the mechanical properties and stability of shellac film (Manee Luangtana-anan et al. 2007 : 687-692).

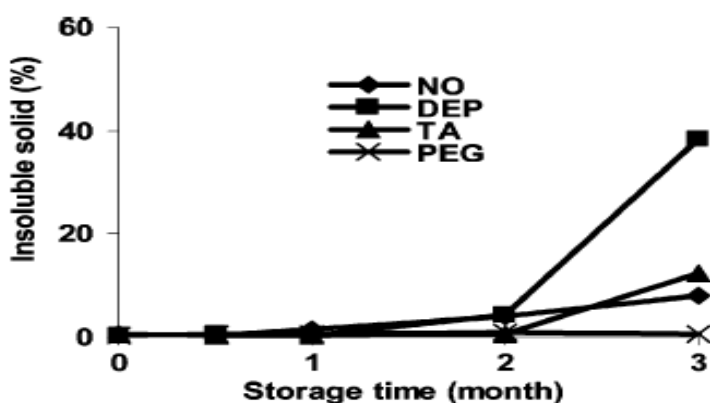


Figure 7 Effect of storage time on insoluble solid of unplasticized (NO) and plasticized shellac films (DEP, TA, PEG) in free acid form (storage at 40 °C, 75% RH)

Source : Manee Luangtana-anan et al., "Effect of salts and plasticizers on stability of shellac film," *Journal of Agricultural and Food Chemistry* 55 (2007) : 690.

Apart from various types of plasticizers, the different molecular weights of plasticizers were also reported to affect on the physicochemical properties and stability of polymer film. The composition, size and shape of a plasticizer as well as its compatibility with the polymer could affect the interactions between the plasticizer and the polymer chain due to its ability to attract water to the plasticized protein films (Sothornvit and Krochta 2001 : 149-155). Plasticizers with characteristics such as smaller size, higher polarity, more polar groups per molecule, and greater distance between polar groups within a molecule generally impart greater

plasticizing effects on a polymeric system (Cheng et al. 2006 : E62-E67). The selection of a plasticizer for a specified system is normally based on the compatibility and permanence of the plasticizer, the amount of necessity for plasticization, and the desired physical properties of the films (Cheng et al. 2006 : E62-E67). The addition of plasticizers i.e., triethyl citrate (TEC) and different molecular weight of polyethylene glycol (600, 1500, 4000, 6000 and 35000) caused a decrease in elastic modulus and glass transition temperature ( $T_g$ ) and increased percentage of elongation at break of free shellac film. This effect was related to the different molecular weights and concentrations of plasticizers (Qussi and Sues 2006 : 403-412). The flexibility of starch films can be improved by the incorporation of plasticizers (Abdorrezza et al. 2011 : 56-60; Galdeano et al. 2009 : 492-498). The major  $T_g$  values of the plasticized starch/decolorized hsian-tsao leaf gum films were relatively independent on the percentage of the added plasticizer (Chen and Lai 2008 : 1584-1595). This was proved that the molecular weight of plasticizer played a crucial role on the stability of polymer film (Manee Luangtana-anan et al. 2010 : 12934-12940). In addition, different molecular weights of PEG had some influences on the stability of shellac films. The insoluble solid was 6 %, 3 %, 0.3 % and 25 % for unplasticized and plasticized shellac with PEG 200, 400 and 4000, respectively after 90 days of storage as shown in Figure 8.

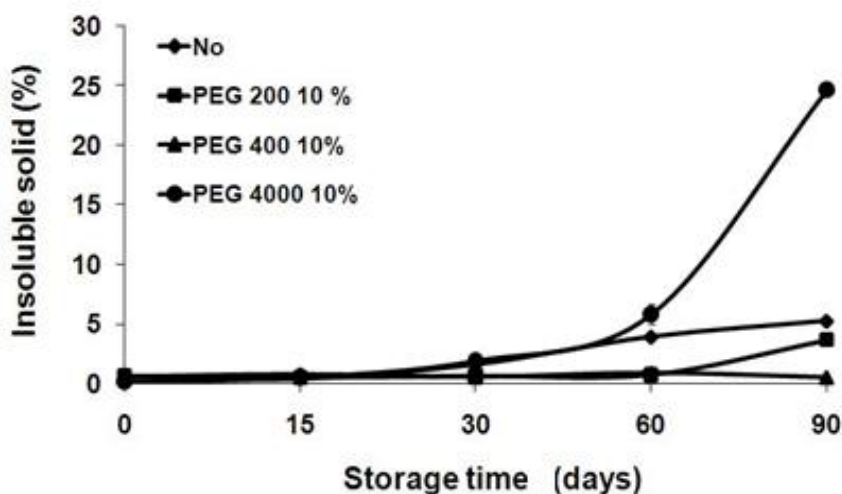


Figure 8 Effect of various polyethylene glycols on insoluble solid (IS) of shellac films after storage at 40 °C, 75% RH for 3 months

Source : Manee Luangtana-anan, Jurairat Nunthanid and Sontaya Limmatvapirat, "Effect of molecular weight and concentration of polyethylene glycol on physicochemical properties and stability of shellac film," Journal of Agricultural and Food Chemistry 58 (2010) : 12941.

The slight change was observed for unplasticized and plasticized shellac with PEG 200 while profound increase was shown for plasticized shellac with PEG 4000 after 90 days of storage. The extremely low insoluble solid was reported for shellac plasticized with PEG 400 (Manee Luangtana-anan et al. 2010 : 1376-1382). The effect of molecular weight of PEG could be explained by the polymerization mechanism as displayed in Figure 9. The polymerization of shellac could be protected by the hydrogen bonding formation between carboxyl or hydroxyl group of shellac and hydroxyl group of PEG. The PEG 200 and 400 could prevent between the polymer chains of shellac from the cross-linking formation of the esterification process and hence insoluble solid was shown lower than unplasticized shellac. However, the PEG 4000 could not perform the protective capability efficiently due to the longer chain of PEG 4000 causing the difficulty in insertion between the polymer networks. The high polarity was obtained when PEG 4000 was used indicated by the high surface free energy tended to accelerate the polymerization

process into a high extent compared with unplasticized shellac. The high polarity was due to the high OH group, contributing to the stronger hydrogen bonding until the closer shellac chain network formed, leading to the enhancement in polymerization. PEG 200 could protect shellac up to 90 days and further storage gave the higher insoluble solid resulting from the loss of plasticizer upon storage. Therefore, PEG 400 was the only plasticizer that could protect shellac from polymerization, indicating the size of plasticizer attributing to the stability of shellac. The optimum molecular weight was required to protect shellac from polymerization (Manee Luangtana-anan et al. 2010 : 12934-12940).

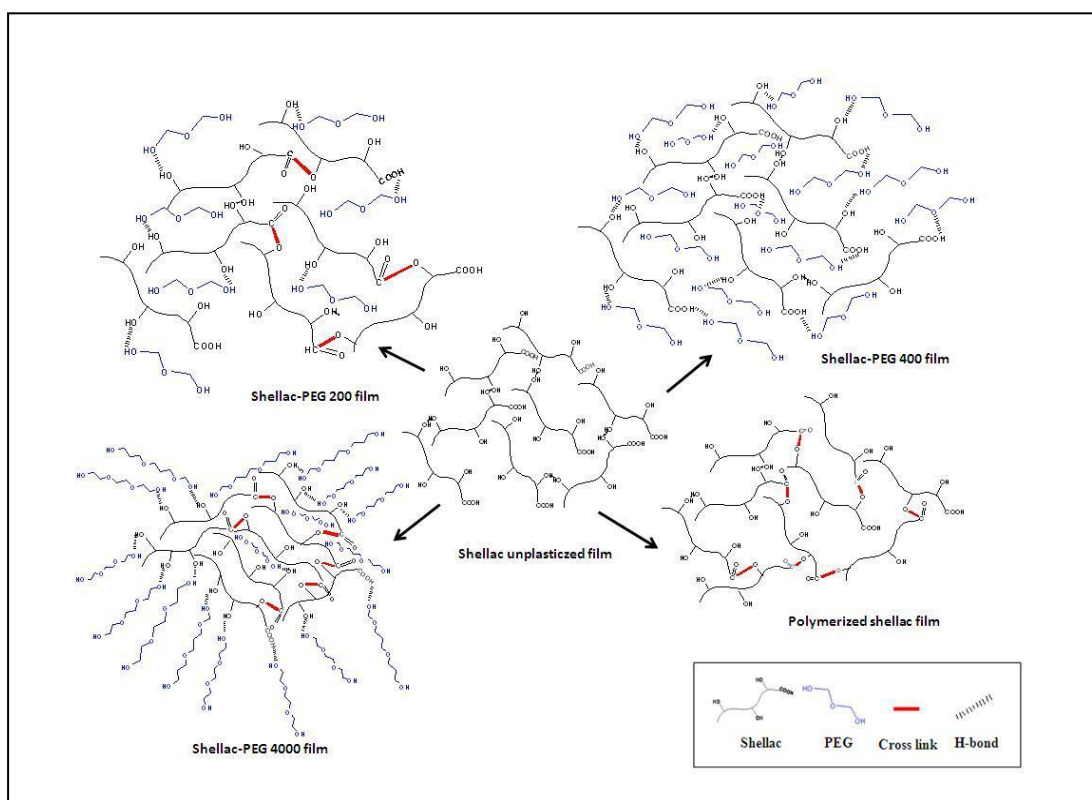


Figure 9 Polymerization propose diagram of unplasticized and plasticized shellac film with PEG (200, 400 4000) after storage at 40 °C, 75% for 3 months

Source : Manee Luangtana-anan, Jurairat Nunthanid and Sontaya Limmatvapirat, "Effect of molecular weight and concentration of polyethylene glycol on physicochemical properties and stability of shellac film," Journal of Agricultural and Food Chemistry 58 (2010) : 12942.

Apart from the types and molecular weights, the concentrations of plasticizers were also reported to affect on the properties of polymer film. The higher glycerol content, the higher water vapor permeability and flexibility of gellan film was obtained, attributing to the higher hydrophilicity of higher concentration of glycerol (Yang and Paulson 2000 : 563-570). The increase in the concentration of polyethylene glycol exhibited the enhancement of the flexibility of shellac film while the reduction of the elastic modulus and glass transition temperature (T<sub>g</sub>) of shellac film (Qussi and Suess 2006 : 403-412). The different concentrations of PEG 400 affected the stabilization of shellac film. PEG 400 at the concentration of 10% (w/w) could prevent the polymerization for only 4 months and the significant change of all parameters was then reported. However, at the higher concentration, 20% (w/w) of PEG 400 could prolong the stability of shellac for 180 days of study (Manee Luangtana-anan et al. 2010 : 12934-12940). Furthermore, the addition of plasticizers affected the change in the film coating efficiency as predicted by two parameter i.e., work of adhesion and spreading coefficient which are based on the calculation of the surface free energy. The higher values of both parameters, the higher efficiency in coating over the substrate surface can be obtained (Oh and Luner 1999 : 203-219). The increase in the concentrations of hydrophilic plasticizers, the decrease in the values of wettability and adhesion coefficients of film coating solution over fruit skins i.e., carrot tomato and mango are obtained. It was attributed to the reduction of film coating efficiency due to the fruit skin are low surface free energy, leading to the low interaction between fruit skin and film coating solution. Therefore, the coating efficiency of polymer film is dependent on the characteristic of surface and the composition of polymer film coating (Casariego et al. 2008 : 1452-1459; Cerqueira et al. 2009 : 372-378).

### **3.3 Salt formation**

From literature review the shellac could be prepared by various salt forms e.g., ammonium, 2-methyl-2-amino 1-propanol (AMP) salts form, Sodium carbonated and composite salt formation between ammonium hydroxide and 2-methyl-2-amino 1-propanol or ammonium hydroxide and 2-Amino 2-methyl 1,3 propanediol (Manee Luangtana-anan et al. 2007 : 687-692; Sontaya Limmatvapirat et al. 2007 : 690-698; Narumol Meenabun et al. 2010 : 467-470).

### 3.3.1 Shellac in ammonium and AMP salts from

The shellac in salt forms e.g., ammonium (AMN) and 2-methyl-2-amino 1-propanol (MAP) salts could protect the stability of shellac better than shellac in free acid form for 3 months of storage which was predicted by the acid value and percentage of insoluble solid. The percentage of insoluble solid of unplasticized shellac film in free acid form was increased after 3 months of storage whereas shellac in both salt forms changed slightly as shown in Figure 10. The percentage of insoluble solid of free acid at 3 months of storage was 8% while of ammonium and MAP salts were 1.2% and less than 1%, respectively, suggesting that the higher polymerization upon storage for shellac in free acid form (Manee Luangtana-anan et al. 2007 : 687).

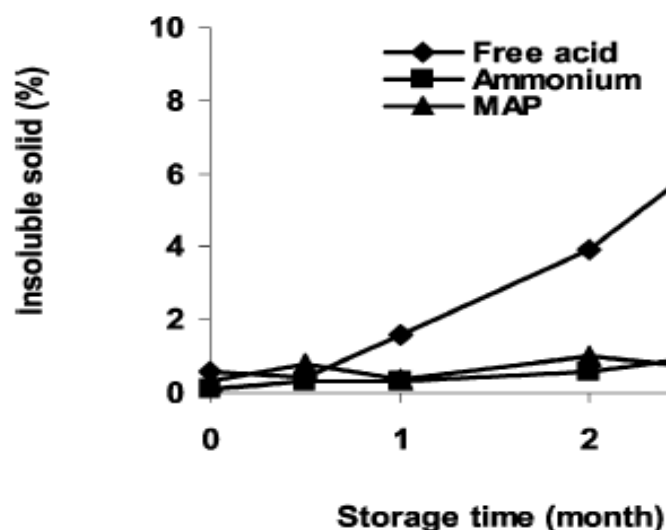


Figure 10 Effect of storage time on insoluble solid (%) of unplasticized shellac films in free acid, ammonium, and MAP forms (storage at 40 °C, 75% RH)

Source : Manee Luangtana-anan et al., "Effect of salts and plasticizers on stability of shellac film," *Journal of Agricultural and Food Chemistry* 55 (2007) : 689.

In addition, shellac is composed of hard resin of polyester which has a lower acid value whereas the soft resin of single resin has a higher acid value. The acid value of shellac is the average value of polyester and single ester. The polyester part tend to polymerize first and to form insoluble solid so that the average

acid value changed slightly during the first 3 months. The higher stability of shellac in ammonium salt form is a result of the protection of ammonium at the carboxylic site of shellac group, attributing to the less polymerization. However, the polymerization could be protected by salt formation with AMN or AMP. The carboxylic acid to carboxylate conversion could increase the solubility and stabilize the shellac. AMP should more strongly interact with the carboxylate, resulting in more ionization, plasticization and stability as compared to AMN. The increase in the interaction was attributed to the hydrogen bond formation between hydroxyl groups of AMP and shellac. In addition, the steric effect of the large molecular size of AMP might cause the polymer chains to separate from each other and reduce the possibility of esterification among polymer chains of shellac (Sontaya Limmatvapirat et al. 2007 : 690-698). The proposed diagram of salt formation of various forms of shellac as displayed in Figure 11.

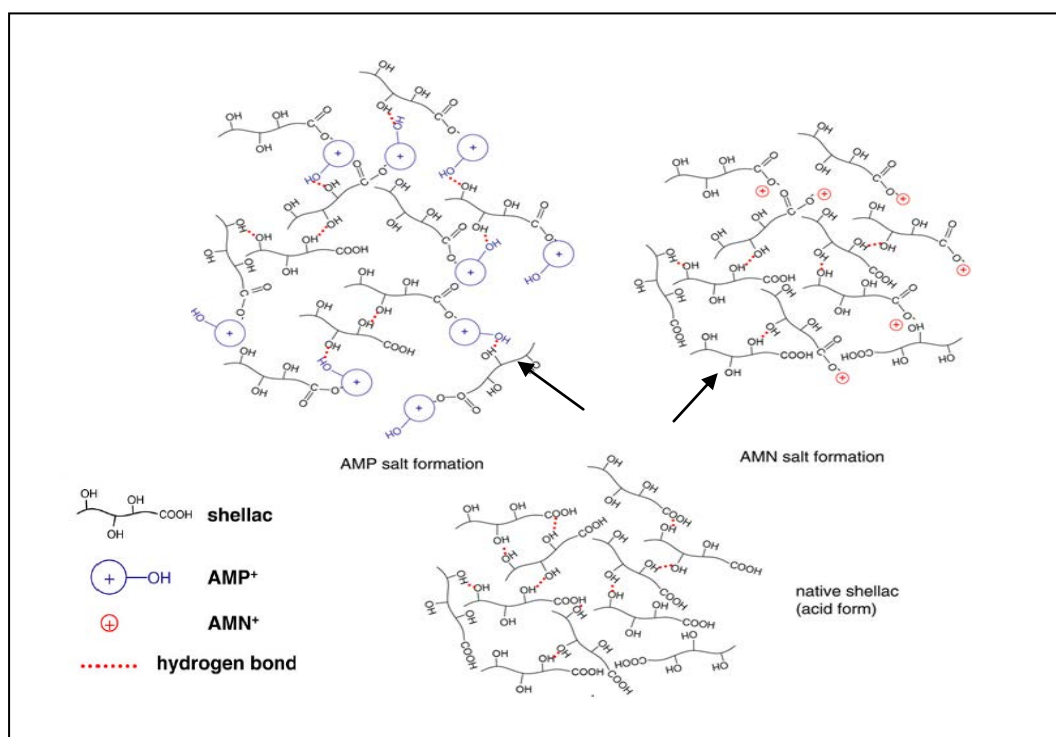


Figure 11 Proposed diagram of salt formation of various forms of shellac

Source : Sontaya Limmatvapirat et al., "Enhanced enteric properties and stability of shellac films through composite salts formation," European Journal of Pharmaceutics and Biopharmaceutics 67 (2007) : 697.

### 3.3.2 Composite salt formation

The stability and solubility are the drawback of shellac due to the polymerization. Limmatvapirat et al. attempted to improve the stability and solubility of shellac by composite salt formation as enhanced the enteric properties. The samples of shellac were prepared by dissolving shellac at various ratios between 2-amino-2-methyl-1-propanol (AMP) and ammonium hydroxide (AMN). The result demonstrated that the higher ratios of AMP: AMN, the higher solubility was obtained, confirmed by the increase in absorbance ratio of the FTIR peaks due to C=O stretching of carboxylate and carboxylic acid due to the higher ionization of AMP salts. Upon storage at 40 °C, 75% RH, the acid value and insoluble solid of AMP salts were relatively constant even after storage over 180 days, suggesting that AMP could protect the polymerization among carboxyl and hydroxyl group of shellac. The percentage of insoluble solid was shown in Figure 12. Therefore, AMP should bind much tighter at the carboxylate binding site as compared with AMN, resulting in the increase in solubility and stability of shellac (Sontaya Limmatvapirat et al. 2007 : 690-698).

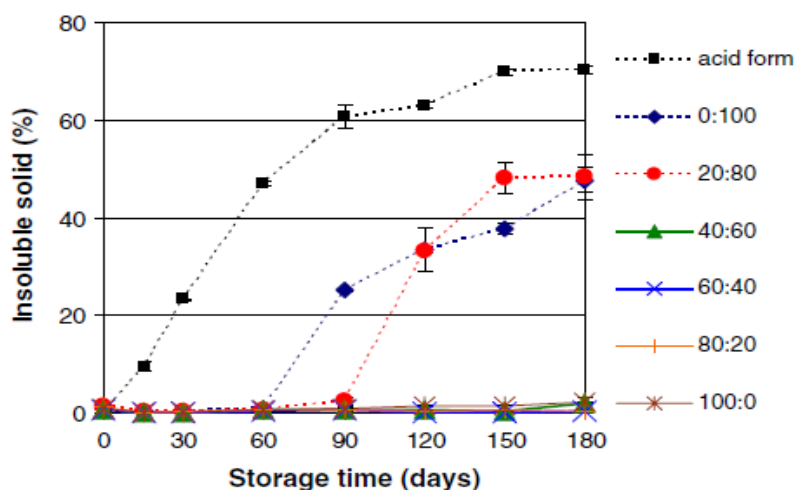


Figure 12 Percent insoluble solid of acid form and various salt forms (AMP : AMN) of shellac after storage at 40 °C, 75% RH for 180 days

Source : Sotaya Limmatvapirat et al., "Enhanced enteric properties and stability of shellac films through composite salts formation," European Journal of Pharmaceutics and Biopharmaceutics 67 (2007) : 695.

### **3.4 Modified shellac**

Modification of shellac with cyclic anhydride is one approach to improve the solubility and stability of shellac. It is due to shellac consists of several hydroxyl groups, attributing to the modification of shellac by esterification with cyclic anhydride, e.g. succinic anhydride. It should be a possible mean for increasing the number of carboxyl groups. Sontaya Limmatvapirat et al. reported that the formation of shellac succinate was obtained by organic solvent reaction. The partial succinate was esterified at the O-H groups of shellac molecules which are detected by various characterization techniques. The increase in succinate amount to shellac polymer affected the film properties such as mechanical properties, pH solubility, water vapor permeability and stability. The film prepared from shellac succinate had higher flexibility, whereas the less modulus was found. In addition, the enhancement of aqueous solubility at the pH of small intestine is observed, exhibiting the modification of shellac could enhance the stability and solubility of shellac for enteric coating application (Sontaya Limmatvapirat et al. 2008 : 335-344).

### **3.5 Composite polymer or blended polymer**

Composite polymer or blend is an effective method for providing a new material as particular in various applications which is designed to take advantages of single components. The mechanical and barrier properties of composite polymer strongly depend on the characteristics of constituted polymer and their compatibility. The composite film obtained from blending of two different polymers can be expected to change physicochemical properties such as water vapor permeability coefficient, mechanical properties, stability and solubility (García et al. 2004 : 339-345; Siepmann et al. 2008 : 1-15). Various combinations of two natural polymers are proteins and polysaccharides, proteins and lipids, polysaccharides and lipids or synthetic polymers and natural polymers (Yu et al. 2006 : 576-602; Bourtoom 2008 : 237-248). Generally, the compatibility of polymer blends is often significantly affected by the interaction between the components of the blends that in turn affects the blends properties. Therefore, a major problem to be concerned for polymer blends is compatibility. It is an advantage that intermolecular interactions exist between two polymer species. The formation of composite polymer could be prepared by varying the ratio of polymer blend as shown in Figure 13.

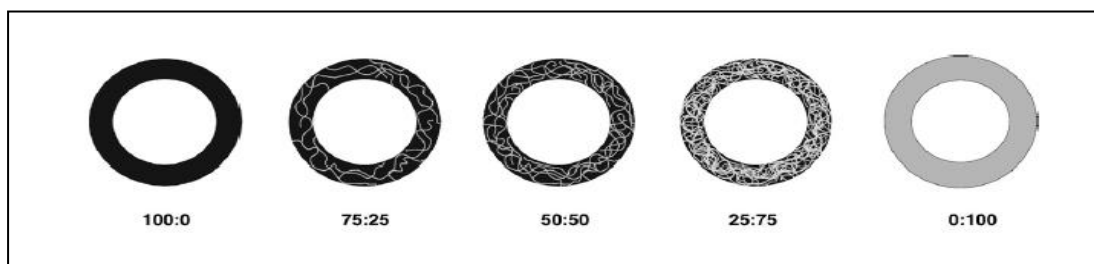


Figure 13 Schematic presentation of the strategy to use composite polymer

Source : F. Siepmann et al., "Polymer blends for controlled release coatings," Journal of Controlled Release 125 (2008) : 2.

Many researches have used the composite polymer to overcome the drawback in limiting usage of shellac for various applications.

Qussi and Suess developed the enteric properties of pellet when coated with aqueous shellac and different hydrophilic polymers i.e., polyvinyl alcohol (PVA), hydroxypropyl methylcellulose (HPMC) and cabomer 940. It was reported that the incorporation of different concentrations of this hydrophilic polymer into shellac coating resulted in the enhancement of pores in the matrix, leading to the increase in the drug release from the pellets in distilled water. Upon storage the shellac coating with hydrophilic showed the good stability indicated by the % percent drug release upon storage for 12 months as shown in Table 1-2 (Qussi and Suess 2005 : 99-108).

Table 1 Stability study of shellac coated pellets containing 10% w/w PVA relative to shellac

Time [hr]	Drug release [%] after months				
	0	3	6	9	12
0	0.0±0	0.0±0.1	0.0±0	0.0±0	0.52±0.01
1	0.31±0.1	0.22±0.2	0.11±0.01	1.0±0.2	1.22±0.02
2	1.35±1	1.8±1	1.55±0.5	2.33±0.6	2.2±0.1
3	1.75±1	2.1±0.5	1.84±0.1	3.52±1	3.1±0.5
4	5.6±1	5.1±1	4.8±1	5.8±1	5.47±3
5	17.89±2	16.32±2	16.5±1	18.7±3	18.22±1
6	40.96±3	37.81±2	38.9±3	40.1±0.5	40.41±2
7	58.1±2	55.44±3	55.0±1	57.5±3	58.3±1
8	78.42±4	76.2±3	79.12±3	80.8±2	80.3±4

Source : B. Qussi and W. G. Suess, "Investigation of the effect of various shellac coating compositions containing different water-soluble polymers on in vitro drug release," Drug Development and Industrial Pharmacy 31 (2005) : 106.

Table 2 Stability study of shellac coated pellets containing 10% w/w HPMC relative to shellac

Time [hr]	Drug release [%] after months				
	0	3	6	9	12
0	0.0±0	0.0±0.1	0.2±0.1	0.0±0	0.32±0.01
1	18.5±2	19.1±0.5	19.4±0.2	19.0±1	20.2±1.2
2	37.3±4	35.3±1	37.6±2	37.42±1.3	37.51±1
3	79.34±4	80.4±2	81.12±2	80.5±1	81.4±4
4	89.2±2.4	90.2±1	90.7±1	91.2±2	91.46±3
5	92.9±3	94.32±1	94.4±1	94.71±1	95.1±0.5
6	93.5±1.5	95.13±2	94.6±2.1	95.3±2	95.9±3
7	94.1±2	95.21±1	95.0±3	95.5±1.3	96.4±2
8	95.3±1	96.2±2	95.33±2	95.4±1.7	96.55±3

Source : B. Qussi and W. G. Suess, "Investigation of the effect of various shellac coating compositions containing different water-soluble polymers on in vitro drug release," Drug Development and Industrial Pharmacy 31 (2005) : 106.

Qussi and Suess improved the mechanical properties and drug permeability of shellac by addition of hydrophilic polymer such as; HPMC, MC and carbomer. It was found that the higher ratios of hydrophilic polymer, the higher percent elongation (Table 3) and drug permeability of shellac film was obtained. It was due to the characteristic nature of HPMC, MC and carbomer was soluble in water

and higher affinity into shellac network and could interact with the shellac molecules in the water (Qussi and Sues 2006 : 403-412).

Table 3 Influence of polymers on the thermal and mechanical properties of shellac films

Polymer additives (w/w based on the mass of shellac)	Young's modulus [MPa] (n = 20)	Elongation at break [%] (n = 20)	Glass transition temperature T <sub>g</sub> [°C] (n = 4)
none	338.4 ± 1.2	3.05 ± 0.6	45.64 ± 2.0
HPMC 10%	214.4 ± 4.0	13.2 ± 2.4	49.2 ± 1.0
HPMC 20%	144 ± 5.0	22.3 ± 1.3	45.72 ± 1.0
HPMC 25%	70.8 ± 3.0	43.0 ± 10.8	43.11 ± 1.2
MC 10%	317.0 ± 12.0	7.0 ± 3.8	44.2 ± 1.0
MC 20%	63.1 ± 5.0	140.3 ± 9.0	35.32 ± 0.5
MC 25%	56.9 ± 3.0	145.2 ± 20.0	35.22 ± 0.5
Carbomer 0.5%	439.8 ± 3.5	3.08 ± 1.1	41.34 ± 1.0
Carbomer 2%	110.2 ± 4.5	31.91 ± 2.9	38.47 ± 1.2
Carbomer 2.5%	60.7 ± 2.6	52.52 ± 5.3	38.43 ± 2.0
PVA 10%	335.0 ± 16.0	4.7 ± 0.5	48 ± 2.0
PVA 20%	489.0 ± 5.0	2.80 ± 1.00	67.34 ± 1.0
PVA 25%	570 ± 14.0	1.50 ± 0.80	71.98 ± 3.0
EC 10%	317.5 ± 3.4	3.3 ± 2.0	48.5 ± 1.0
EC 20%	360.1 ± 4.0	2.8 ± 2.3	48.92 ± 0.5
EC 25%	365.4 ± 5.3	2.1 ± 2.1	49.02 ± 0.5

Source : B. Qussi and W. G. Sues, "The influence of different plasticizers and polymers on the mechanical and thermal properties, porosity and drug permeability of free shellac films," Drug Development and Industrial Pharmacy 32 (2006) : 408.

Stummer et al. attempted to improve the enteric properties of shellac and developed probiotic formulations that contained natural polymer. The effects of water-soluble polymers such as sodium alginate, hydroxypropyl methylcellulose and polyvinylpyrrolidone on physical properties and coating properties of shellac were evaluated. The addition of hydroxypropyl methylcellulose and polyvinylpyrrolidone had superior miscibility with shellac compared to sodium alginate. The incorporation of some hydrophilic polymer gave the increase in water solubility and swelling at pH 1.2, 6.8 and 7.4 leading to the enhancement of an enteric coating efficiency. Then, three fluid bed dried bacterial species i.e., *Enterococcus faecium*, *Bifidobacterium bifidum* and *Lactobacillus reuteri*, were coated with formulations comprising different concentrations of shellac and additives. The coatings with shellac containing 5% sodium alginate or up to 20% w/w polyvinylpyrrolidone could protect the

microorganisms against acidic pH and provided the best release profile in simulated intestinal fluid (Stummer et al. 2010 : 1312-1320).

Kojima, Ogawa and Kohayakawa studied the effect of shellac content on the physicochemical properties of cornstarch blend. The increase in shellac concentrations within cornstarch network caused the decrease in the water solubility and the change in the crystallinity of composite polymer resulting from the complex formation between shellac and cornstarch as shown in Figure 14 (Kojima, Ogawa and Kohayakawa 2000 : 13-19).

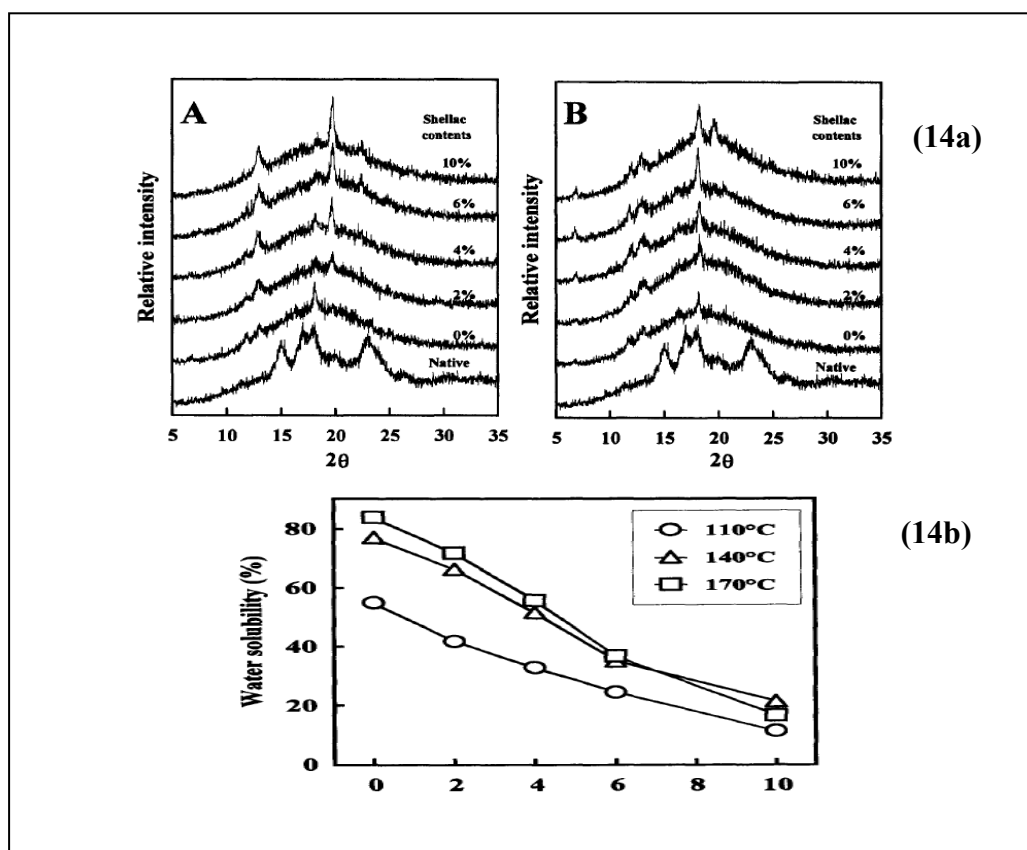


Figure 14 Effect of shellac content on powder X-ray diffraction pattern (14a) and water solubility of corn starch extrudates (14b)

Source : M. Kojima, K. Ogawa and K. Kohayakawa, "Effect of shellac on some physicochemical properties of cornstarch extrudates," Journal of Applied Glycoscience 47 (2000) : 16-17.

#### 4. Hydrocolloid polymers

Hydrocolloids polymers have long been widely used in food and pharmaceutical industries as various applications such as, thickening agent, gelling agent, stabilizing agent, emulsifiers and film forming agent (Dickinson 2009 : 1473-1482). Generally, the hydrocolloid polymers can be classified in three groups including;

(1) Natural hydrocolloids polymer which is derived from natural sources materials such as agar, carrageenan, gelatin, pectin, chitin, starch and alginate, etc.

(2) Modified natural hydrocolloids polymer which is obtained from adding natural hydrocolloid polymer and adding with some function group e.g. chitosan and derivatives, cellulose and derivatives, etc.

(3) Synthetic hydrocolloids polymer which is obtained from chemical reaction e.g. polyethylene oxide polymers (Nishinari et al. 2000 : 195-201).

In addition, the hydrocolloid polymer has been extensively used in edible film coatings due to the effectiveness for barrier properties such so as to gas, moisture, good mechanical property and higher stability (Chen and Nussinovitch 2001 : 127-137; Bourtoom 2008 : 237-248; Phan The et al. 2009 : 691-699). Thus, the types of food products have been coated with the hydrocolloids polymer as prevent the loss of moisture, increase the texture of products and maintain color attributing to the consequently extended the shelf-life of food products (García et al. 2004: 339-345; Bourtoom. 2008 : 237-248; Lopez-Rubio and Lagaron 2011 : 997-1004) and has been widely used in pharmaceutical product for stability enhancement of vitamin C or drug and controlled drug release (Satit Puttipipatkachorn et al. 2001 : 143-153; Shu and Zhu 2002 : 235-243). Various hydrocolloids have been tested as edible film coating material such as hydroxypropyl methyl cellulose, methyl cellulose, pectin, alginate, carrageenan, locust bean gum gellan gum gelatin and soy protein (Lee et al. 2004 : 251-254; Cheng et al. 2006 : E62-E67; Dong et al. 2006 : 37-44; Casariego et al. 2008 : 1452-1459; Abdorreza et al. 2011 : 56-60).

## 5. Gelatin

Gelatin, a natural hydrocolloid polymer, is obtained from hydrolysis of collagen from skin, bones and connective tissue of pig or fish (Li et al. 2006 : 544-549; Gámez-Guillín et al. 2009 : 3-16). The structure of gelatin made from bovine and fish skin consists of many amino acids that containing carboxyl groups and amino group on backbone chains as shown in Table 4. Generally, gelatin can be classified in two groups including; gelatin type A which is derived from acid-cured tissue and gelatin type B which is derived from lime-cured tissue. Gelatin type A has 78-80 millimoles of free carboxyl groups per 100 g of protein and pI of 7.0-9.0 while type B has 100-115 millimoles of free carboxyl groups per 100 g of protein and pI of 4.7-5.2. The pH of a 1.5% solution at 25 °C is 3.8-5.5 for Type A and 5.0-7.5 for Type B (Badii and Howell 2006 : 630-640; Karim and Bhat 2009 : 563-576).

Gelatin is a protein widely used in food, agro, pharmaceutical, and cosmetic industries (Vanin et al. 2005 : 899-907; Gámez-Guillín et al. 2009 : 3-16), which is one of the materials used in the edible film coating, due to the abundance of raw material, biodegradability, biocompatibility, low cost, global availability, excellent film forming and good mechanical properties (Arvanitoyannis et al. 1998 : 371-382; Vanin et al. 2005 : 899-907). The physical properties and structural of gelatin are mainly influenced by the molecular weight distribution and amino acid composition which is changed by the chemical structure at side chain of gelatin and the condition of medium i.e., acid or base. The change in medium results in the change in the ionization of amino acid at carboxyl and amino groups thus affecting the physicochemical properties of gelatin such as solubility and mechanical properties, etc. Among natural polymers, gelatin is probably the most analogous to a synthetic polymer due to linear structure, fairly limited monomer composition and its polydispersity (Sobral and Habitante 2001 : 377-382; Sobral et al. 2001 : 423-432).

Table 4 Amino acid composition (g amino acids/100 g of protein) for gelatins between bovine hide and pigskin

	Bovine hide	Pigskin
Alanine	12.92	10.08
Arginine	4.80	4.01
Aspartic acid	7.31	6.76
Glutamic acid	11.98	11.12
Phenylalanine	2.00	1.99
Glycine	22.16	22.60
Histidine	0.73	0.72
Isoleucine	1.82	1.33
Leucine	2.73	2.54
Lysine	3.87	3.50
Methionine	0.66	0.68
Proline	3.29	2.21
Serine	3.26	7.63
Tyrosine	0.40	0.62
Threonine	1.78	1.35
Valine	2.37	4.84
Amonium	7.68	9.60

Source : P. J. A. Sobral et al., "Mechanical, water vapor barrier and thermal properties of gelatin based edible films," Food Hydrocolloids 15 (2001) : 424.

## 6. Composite polymer with gelatin

The drawbacks of biopolymer film such as poor mechanical properties, barrier properties and instability can be improved by the formation of composite polymer with gelatin which has an excellent film forming, good mechanical properties and is easily blended with other polymer. The potential to blend with other polymers is found, due to its ability from the interaction (Xiao et al. 2001 : 1596-1602; Cheng et al. 2003 : 2871-2880; Dong et al. 2006 : 37-44; Li et al. 2006 : 544-549; Farris et al. 2011 : 61-70). Many researches have widely utilized gelatin as a secondary polymer in the formation of composite polymer i.e., soy protein-gelatin, alginate-gelatin, gellan-gelatin, chitosan-gelatin, konjac glucomannan-gelatin and pectin-gelatin so as to improve some properties of edible film (Jia-hui et al. 1999 : 476-476; Xiao et al. 2001 : 1596-1602; Cheng et al. 2003 : 2871-2880; Lee et al. 2004 : 251-254; Dong et al. 2006 : 37-44; Cao et al. 2007 : 1153-1162; Farris et al. 2011 : 61-70).

Cao et al. found that the higher gelatin content, the higher tensile strength and the higher percent elongation as obtained, leading to the increase in the mechanical strength and flexibility of soy protein film. The result may be due to the hydrogen bonding between amino and carboxyl of soy protein and gelatin. Furthermore, the mechanical properties i.e., tensile strength and percent elongation of soy protein and gelatin composite film was dependent on pH, thermal and ionic strength as shown in Figure 15 (Cao et al. 2007 : 1153-1162).

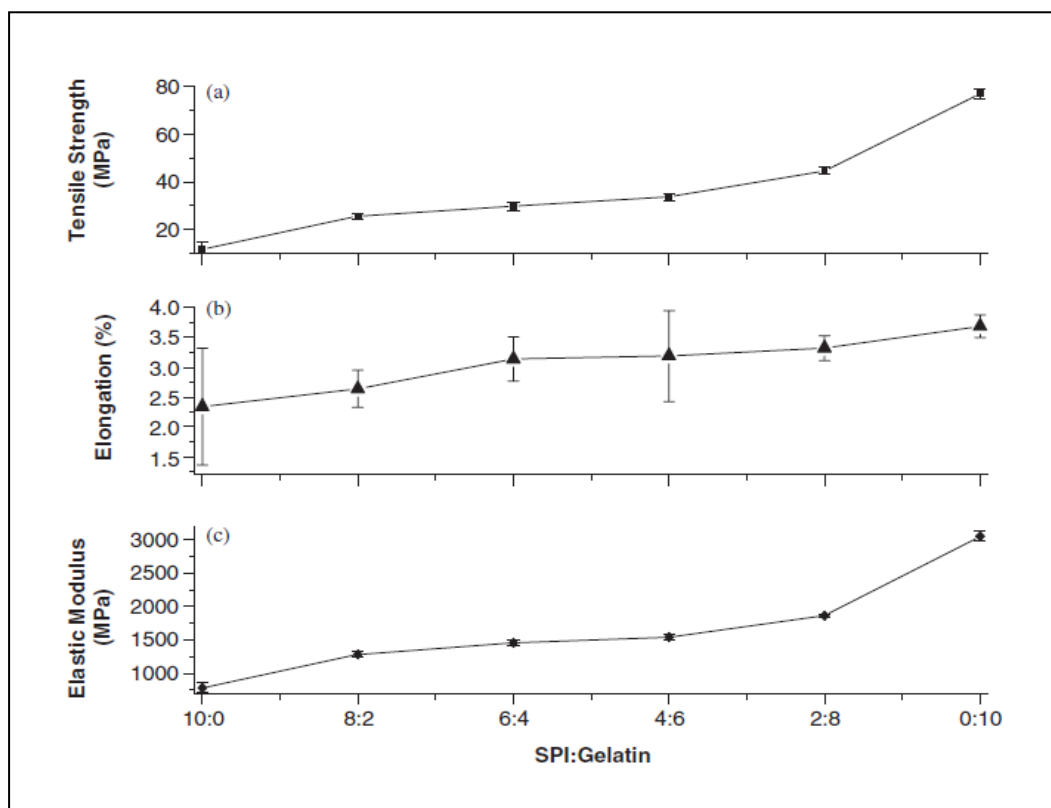


Figure 15 Effect of gelatin content on mechanical properties of soy protein film

Source : N. Cao, Y. Fu and J. He, "Preparation and physical properties of soy protein isolate and gelatin composite films," *Food Hydrocolloids* 21 (2007) : 1155.

Cheng et al. reported that the higher gelatin content contributed to the higher percentage of elongation, leading to the increase in the flexibility of chitosan film while reduced the mechanical strength of chitosan film. The decrease in strength of chitosan blend was due to the reduction of hydrogen bonding of chitosan as the gelatin concentrations increased. This result was proved by the FTIR spectroscopy,

powder X-ray diffraction and thermal analysis. In addition, the increase in gelatin content led to the increase in wettability of composite film, indicated by the reduction of contact angle when water was used as a wetting liquid (Cheng et al. 2003 : 2871-2880).

Rivero et al. demonstrated the incorporation of chitosan within gelatin network contributed to the increase in the stronger film while reduced the water vapor permeability of gelatin film leading to the higher protective efficiency in edible film packaging (Rivero et al. 2009 : 531-539).

Lee et al. observed that the tensile strength of gellan and gelatin composite film was decreased as increasing the gelatin concentrations whereas the tensile elongation of film was increased when the proportions of gelatin increased (Lee et al. 2004 : 251-254).

Li et al. found that the interaction between konjac glucomannan and gelatin molecular chains was caused by hydrogen bonding, confirmed by FTIR spectroscopy and thermal analysis. The interaction between konjac glucomannan and gelatin is caused the increase in the strength and the flexibility of composite film. Therefore, the mechanical properties of konjac glucomannan could be improved by composite film with gelatin (Li et al. 2006 : 544-549).

Dong et al. reported that the use of gelatin as a secondary polymer for improved the drawback of alginate film. They indicated that the increase in gelatin content contributed to the higher mechanical strength and the higher flexibility due to the interaction between alginate and gelatin which indicated by FTIR spectroscopy as shown in Figure 16. The characteristic absorption bands of gelatin at  $1653\text{ cm}^{-1}$ ,  $1546\text{ cm}^{-1}$  and  $1236\text{ cm}^{-1}$  represented Amide I (C-O and C-N stretching vibration), Amide II and Amide III (mainly N-H bending vibration and C-N stretching vibration), respectively. Finally, the wide absorption band around  $3421\text{ cm}^{-1}$  was due to the stretching vibration of O-H bonded to N-H. The FT-IR spectra of composite film showed the characteristic absorption bands at  $1653\text{ cm}^{-1}$  and  $1546\text{ cm}^{-1}$  of gelatin shifted to lower wave number at  $1642\text{ cm}^{-1}$  and  $1535\text{ cm}^{-1}$ . The absorption band around  $3421\text{ cm}^{-1}$  indicated the stretching vibration of N-H group bonded to O-H group and shifted to a lower wave number at  $3411\text{ cm}^{-1}$ . The change in spectra was

due to the increase in the hydrogen bonding between alginate and gelatin, leading to the increase in the mechanical strength of composite film (Dong et al. 2006 : 37-44).

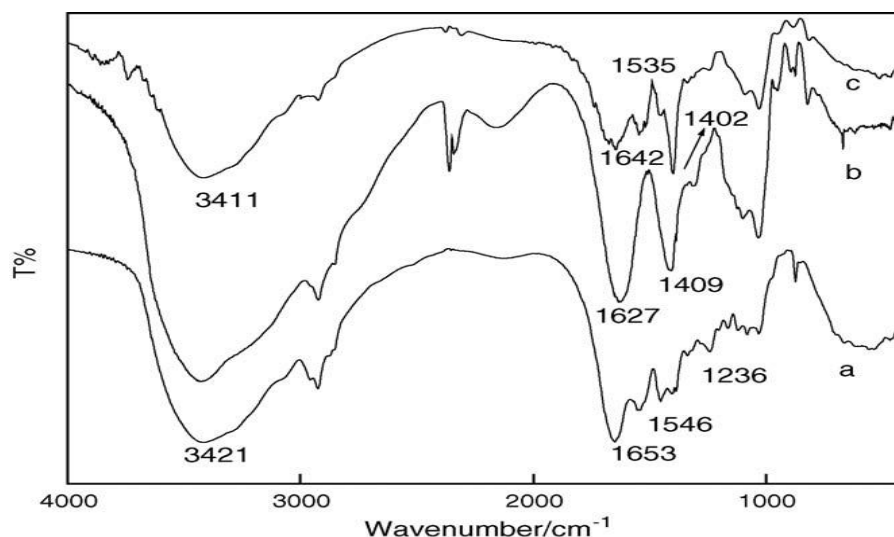


Figure 16 FTIR spectra of gelatin (a), alginate (b) and blend film (c)

Source : Z. Dong, Q. Wang and Y. Du, "Alginate/gelatin blend films and their properties for drug controlled release," *Journal of Membrane Science* 280 (2006) : 39.

## 7. Evaluation of film coating efficiency

The optimization of the coating solutions based on the ability to spread over a substrate surface can be made with four parameters that consist of wettability, surface free energy, work of adhesion and spreading coefficient. The wettability and surface free energy are the most important properties, predicting the capacity of a solution to coat a substrate surface (Cerqueira et al. 2009 : 372-378; Lima et al. 2010 : 101-109).

Apart from wettability and surface free energy, the work of adhesion and spreading coefficient are parameter to predict the film coating efficiency of liquid solution which can calculate based on the contact angle measurement of known surface free energy of coating liquid over substrates (Oh and Luner 1999 : 203-219). The surface free energy is the energy used to expand surface area by  $1 \text{ cm}^2$ , which can be controlled the factor in the processes including wetting and coating of surface. The higher values of work of adhesion and spreading coefficient, the higher efficiency in coating over the substrate surface can be obtained. There are some publishes reported

the evaluation of film coating over food and pharmaceutical products which are based on the contact angle measurement (Casariego et al. 2008 : 1452-1459).

Ribeiro et al. investigated the efficiency of film coating over strawberry surface which found that the strawberry surface was a low energy surface with a surface free energy of 28.94 mN/m, and polar and dispersive components of 5.95 and 22.99 mN/m, respectively. The surface free energy of strawberry surface was calculated by the contact angle measurement of four different standard liquids, i.e., distilled water, formamide bromonaphthalene and toluene at 25 °C using Wu harmonic method equation (Ribeiro et al. 2007 : 63-70) as shown in Figure 17.

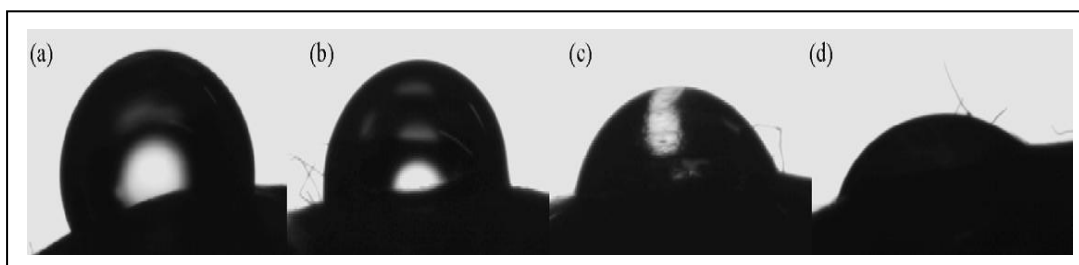


Figure 17 Contact angle of the tested liquids on strawberry surface: (a) water; (b) formamide; (c) bromonaphthalene; (d) toluene

Source : C. Ribeiro et al., "Optimization of edible coating composition to retard strawberry fruit senescence," *Postharvest Biology and Technology* 44 (2007) : 66.

Casariego et al. demonstrated that the tomato and carrot skins were low surface free energy surfaces which had a surface tension about 28.71 and 26.48 mN/m, respectively and had the polar and dispersive components about 3.04 and 25.67mN/m for tomato and 0.34 and 26.13 mN/m for carrot, respectively. The increase in concentrations of chitosan and plasticizers attributed to decrease in the wettability of chitosan film solution over fruit skins, leading to the lower work of adhesion and spreading coefficient due to the low interaction between film coating and fruit surface (Casariego et al. 2008 : 1452-1459).

Oh and Luner reported that the surface free energy parameters of ethylcellulose (EC) films were determined using the Lifshitz–van der Waals: acid-base method and the influence of plasticizers on their surface free energy was also

investigated. The film samples were prepared by dip-coating glass slides in organic solvents containing EC and the contact angles of pure liquids drops on the EC films were measured with a contact angle using the captive drop technique. EC has the lower surface free energy than cellulose. The acid-base (AB) term made only a slight contribution to the total surface free energy. The additions of plasticizer including dibutyl sebacate and dibutyl phthalate resulted in the small decrease in the total surface free energy. The surface free energy affect the interaction of the EC films with other surfaces based on interfacial tension, work of adhesion and spreading coefficient. The consideration of work of adhesion and spreading coefficient based on surface free energy parameters may have potential used to predict the factors affecting on film adhesion and optimization in pharmaceutical film coating (Oh and Luner 1999 : 203-219).

Khan et al. studied the surface free energy of film coating formulations based on hydroxypropyl methylcellulose and containing microcrystalline cellulose, lactose and Tween 20, respectively. The spreading coefficients of the coating formulations were determined on a model tablet surface. The determinations of spreading coefficients were high and positive indicating that the spreading and wettability could not control the various factor in the formation of film coating. The adhesion of the coats to the core was measured. It was found that the addition of some additives had an influence on the adhesion of the film. The maximum adhesion was reported as the incorporation of microcrystalline cellulose in coating formulation giving the strong interaction with the tablet core. In addition, adhesion was enhanced when the tablet cores were made at a higher compaction force. Atomising air pressure had little influence on the adhesion (Khan et al. 2001 : 113-119).

## **8. Applications of shellac coating for food and pharmaceutical industries**

The shellac has been widely used in food industries and agro industries for water, gas, lipid and microbial spoilage protection and hence prolonging the shelf-life of products (Hagenmaier and Baker 1993 : 283-287; McGuire and Hagenmaier 1996 : 100-106; Valencia-Chamorro et al. 2009 : 72-79) and has been used for moisture protection of drugs, controlled delivery and enteric coating for drug and probiotic (Sontaya Limmatvapirat et al. 2004 : 41-49; Pearnchob et al. 2004 : 313-321;

Stummer et al. 2010 : 1312-1320) in pharmaceutical industries. There are some published reports on the fruit and vegetable coating with shellac.

Bai et al. reported that the apples coating with the various formulations such as, single shellac, candelilla and shellac-carnauba wax. The coated apples were detected upon storage for 2 or 4 weeks at 20.8 °C. The physicochemical properties of fruit such as gas permeability, surface gloss, weight loss, flesh firmness, Brix, titratable acidity and ethanol content were investigated. The results indicated that all coating attributed to the maximum fruit gloss, lowest internal O<sub>2</sub>, highest CO<sub>2</sub>, and least loss of flesh firmness for all of the varieties. However, the coating formulation was depended on the type of apple and the characteristic skin of fruit (Bai et al. 2003 : 381-390).

Pongpen Accaseavorn et al. developed shellac based fruit coating for extending the shelf-life of mangosteen and Lime (CV. Pan). The technique of shellac coating was prepared by spray-coated technique. A shellac-based fruit coating formula, "Lab-A" was investigated on mangosteen and lime (CV. Pan) when compared to a commercialized coating formula (Teva). The samples of fruit with and without coating were kept in 25 °C, 70 % RH. The fruit coating with Lab A formulation represented the superior qualities when compared to Teva and control formulation, respectively. Therefore, the coating of mangosteens and limes with Lab-A preserved qualities of the fruits for 28 and 56 days at optimum temperature which were 14 and 41 days longer than those at room temperature (Pongpen Accaseavorn et al. 2006 : 42-45).

Qussi and Sues investigated the coating formulation of drug pellets with aqueous shellac containing different amounts of polyvinyl alcohol, hydroxypropyl methylcellulose, and carbomer 940. The coating level needed for enteric coating was determined. The influence of different amounts of PVA, HPMC, and carbomer on drug release and mechanism; the porosity, and the stability of shellac coatings was determined. The incorporation of different concentrations of HPMC within shellac coatings, due to the increase in pores, could increase the drug release from the pellets in the water. The swelling effect of carbomer 940 led to increase in diffusivity of shellac coatings in the water. In addition, PVA was attributed to the small cracking in the films and much more diffusion of drug in the water. All coating systems

containing different hydrophilic polymers which were used in the present work could prevent the dissolution of drug in simulated gastric fluid for 2 hours. However, a rapid and complete release of drug within 45 minutes was observed in simulated intestinal fluid. Drug release from shellac coated pellets and ones containing different amounts of carbomer was affected between 90-180 days, whereas shellac coatings containing different amounts of PVA or HPMC showed the same dissolution profiles with small deviation after 12 months indicating the stability of pellets when coating with shellac and other hydrophilic polymer (Qussi and Sues 2005 : 99-108).

Pearnchob et al. reported that the disintegration improvement of shellac-coated soft gelatin capsules in simulated intestinal fluids (phosphate buffer pH 6.8) by the addition of organic acids and hydrophilic polymers, while retaining gastric resistance. The addition of additives into shellac decreased the disintegration times at phosphate buffer pH 6.8, while the behavior in 0.1 N HCl did not change. In addition, the hardness and disintegration of shellac-coated soft gelatin capsules were monitored by the whole disintegration experiments. The suitable disintegration was obtained when the sorbic acid into shellac-coated soft gelatin capsules was added. Sorbic acid remained in the shellac coating at low pH, but leached in pH 6.8 buffer, resulting in good gastric resistance and rapid disintegration in simulated intestinal fluids. The disintegration time of ethanolic shellac-coated soft gelatin capsules decreased as the amount of pore-former increased. Hence, the slow disintegration of aqueous shellac-coated soft gelatin capsules could be improved by the addition of hydrophilic polymers, such as hydroxypropyl methylcellulose (HPMC). However, higher HPMC concentrations were required in comparison to sorbic acid (Pearnchob et al. 2004 : 313-321).

## CHAPTER 3

### MATERIALS AND METHODS

#### 1. Materials

Shellac was obtained from Union Shellac Part., Ltd. (Bangkok, Thailand). Gelatin (Type A) made from porcine skin was purchased from Sigma Aldrich (USA). The solvents and chemical reagent including, ethanol, ammonium hydroxide, sodium hydroxide, sulfuric acid, potassium dihydrogen phosphate, phenol were obtained from Merck (Germany) while formamide and diiodomethane were purchased from Sigma (USA). Calcium chloride anhydrous was obtained from Carlo Erbra (Germany). Plasticizers used were diethyl phthalate (DEP) from the British Drug House (BDH) Chemicals (UK) and polyethylene glycol 400 was purchased from Sigma (USA). Banana (*Musa* AAA group) cv. Kluai Hom Thong was harvested at 75–80% maturity from a commercial plantation in Nakornpratom, (Thailand).

#### 2. Equipments

1. Aluminium covers (Perkins, P/N SSC0000E030 open sample pan, Japan)
2. Aluminium crimping (Perkins, P/N SSC0000E032 crimping cover, Japan)
3. Analytical balance (Sartorius CP 224s, Germany)
4. Analytical balance (Sartorius, CP224s, Germany)
5. Centrifuge (Hettich, Universal 620 R, Germany)
6. Desiccators (Biologix Research Company, USA)
7. FTA 1000 drop shape instrument (First Ten Angstroms, USA)
8. Fourier transform infrared spectrophotometer (Nicolet 4700, USA)
9. Hot air oven (Heraeus, UT 6060, Germany)
10. Loss on drying measurement (Sartorius Moisture balance, Germany)
11. Magnetic stirrer and Magnetic bar (Mettler-toledo GmbH, Germany)
12. pH meter (Mettler Toledo seveneasy, Switzerland)

13. Scanning electron microscope (model MX 2000, United Kingdom)
14. Schott DURAN (250, 500, 1000 ml)
15. Shaker incubator (SL SHEL LAB, SI4-2, USA)
16. Stability chamber (HOTPACK,model 317332 M, USA)
17. Texture analysis (TA.XT. Plus, UK)
18. Thickness meter (Minitest 600B, Typ 80-121-0306, Germany)
19. UV-VIS spectrophotometer (Agilent, 1100 series, USA)
20. Viscometer (Brook field digital viscometer, DV-III ULTRA, USA)
21. Water bath (SANYO, Walk-Ins, Japan)
22. Water vapor permeable cell
23. Powder X-ray diffractometer (Rigaku, MiniflexII, Japan)

### **3. Methods**

#### **3.1 Preparation and characterization of composite polymer of shellac with gelatin**

The composite polymer of shellac with gelatin was prepared in free film by casting method. The 6% w/w shellac was dissolved in ammonium solution to prepare shellac in ammonium salt form. The amount of 28 % w/w ammonium salt solutions ( $\text{NH}_3$ ) was calculated on the basis of acid value of shellac that the amount of salt used to interact with acid group of shellac. The shellac solution was then centrifuged for 10 min at 6,000 rpm and insoluble solid was removed by Whatman paper filtration with the aid of vacuum pump. The method used was according to Sontaya Limatvapirat et al. (Sontaya Limmatvapirat et al. 2007: 690-698). The 6% w/w gelatin was prepared by hydration in water at 25 °C for 30 min and then dissolved at 50 °C with stirring at the rate of 650 rpm for 1 h. The pH of shellac solution was dependent on the amount of ammonia solution. The 6% w/w composite solutions were prepared by adding different concentrations of gelatin at 10, 20, 30, 40 and 50% w/w into shellac solution. The composite polymer solutions were homogenized by magnetic stirrer for 2 h and then were evaluated for the pH, surface tension and viscosity of composite polymer solutions as described in 3.1.1-3.1.3. All composite solutions were then poured on a glass plate which its surface was treated with silicone solution (Aquasil<sup>®</sup> Siliconizing Fluids) to help peeling and were allowed

to dry at 50 °C for 6-8 hr by hot air oven. The composite polymer was kept in a desiccators containing dried silica gel for 1 h to control the moisture for all films prior to test. The composite polymer films were evaluated for physicochemical properties as described in 3.1.4-3.1.17.

### **3.1.1 pH**

The pH of all composite polymer solutions was measured using pH meter (Mettler Toledo seveneasy, Switzerland). The average of three measurements was performed.

### **3.1.2 Surface tension**

The surface tension of all composite polymer solutions was measured by the sessile drop method using a drop shape instrument FTA 1000 high performance image processing (First Ten Angstroms, USA). The average of three measurements was performed.

### **3.1.3 Viscosity**

The viscosity of all composite polymer solutions was investigated by viscometer (Brook field digital viscometer, DV-III ULTRA, USA). The average of three measurements was performed.

### **3.1.4 Films thickness**

The film thickness (0.160-0.200 mm) was determined at ten points by using a thickness gauge Mini-Test 600 (ElektroPhysik Dr. Steingroever GmbH & Co.KG, Germany).

### **3.1.5 Acid value (AV)**

The acid value was determined by acid-base titration method adapted from United States Pharmacopeia USP XXIII (USP 1995). An accurate weight of 2 g of composite polymer was dissolved in ethanol for overnight and finally adjusted to the total weight of 26 g with ethanol. The solution was centrifuged for 10 min at 4000 rpm. The 26 g of filtrate was titrated with 0.1 N sodium hydroxide. The end point was determined by potentiometric titration instead of using a color indicator due to the dark color of shellac. The graph between milliliters of NaOH and pH was plotted and the acid value was calculated from the value of midpoint of the sharp change of pH. The acid value was expressed as milligram of potassium hydroxide for neutralization of free carboxyl group of shellac (Equ.1). The acid value of shellac was

calculated based on the ratio of shellac in the composite polymers, predicting the amount carboxyl groups of shellac. The average of three measurements was performed.

$$AV = (\text{ml NaOH} \times 56.11) / (40 \times W) \dots \dots \dots \text{Equ.1}$$

Where W was the accurate weight of shellac.

### 3.1.6 Percentage of insoluble solid (IS)

An accurately weighed 1 g of composite polymer sample ( $W_0$ ) was dissolved in 2 % w/w of ammonia solution for overnight and then heat at 37 °C for 2 hr. The insoluble solid on filter paper was dried at 70 °C until the dried weight was constant ( $W_1$ ). The percentage of insoluble solid was calculated from the weight difference of filter paper that was dried at 70 °C before and after filtration (Equ.2). The average of three measurements was performed.

$$\% \text{ IS} = \frac{(W_1 - W_0)}{W_0} \times 100 \dots \dots \dots \text{Equ.2}$$

Where  $W_0$  and  $W_1$  were the accurate dried weight before and after the test, respectively.

### 3.1.7 Fourier transformed infrared spectroscopy

The functional group of all composite polymer were determined by FTIR spectroscopy (Nicolet 4700, Thermo Electron Corporation, USA) using the KBr disc method. Each sample was ground and dried over silica gel. The ground sample was gently triturated with KBr powder and then compressed into a disc with a pressure of 5 tons. Three scans were done for each sample, from a spectral range 400-4000  $\text{cm}^{-1}$  and a resolution of 4  $\text{cm}^{-1}$ . All samples were performed in duplicate.

### 3.1.8 Thermal analysis

Thermal analysis of all composite polymers was measured by differential thermal analysis (DTA) using a Shimadzu differential thermal analyzer equipped with a liquid  $\text{N}_2$  cooling accessory and connected to an IBM/PC and a Hewlett-Packard plotter. Hermetically sealed aluminum pans were used with an empty aluminum pan as reference. The sample size for DTA was approximately 10-20 mg. The measurement was performed between 25-250 °C at a heating rate of 10 °C/min.

### 3.1.9 Morphology

Surface and cross section of all composite polymer films were measured using scanning electron microscope (SEM, model MX 2000, Cam Scan, Cambridge, United Kingdom). The samples were coated with a fine gold layer before obtaining the micrographs. The accelerating voltage was used at 10 kV.

#### 3.1.10 Wettability and surface free energy

The wettability and surface free energy of all composite polymer films were determined by contact angle measurements which were carried out by the sessile drop method using a drop shape instrument FTA 1000 high performance image processing (First Ten Angstroms, USA). The surface free energy of all films, their components and percent polarity were determined based on the contact angle measurement of three different standard liquids which the values of surface free energy and their components were known, i.e., distilled water, formamide and diiodomethane at 25 °C using Wu harmonic method equation (Wu 1982) as follows. All samples were performed in triplicate which was calculated using the following equations (Equ. 3-4).

$$\gamma^T_s = \gamma^D_s + \gamma^P_s \dots \dots \dots \text{Equ.3}$$

$$(1+\cos\theta) \gamma^T_s = [4 (\gamma^D_s \gamma^D_L) / (\gamma^D_s + \gamma^D_L) + 4 (\gamma^P_s \gamma^P_L) / (\gamma^P_s + \gamma^P_L)] \dots \dots \dots \text{Equ.4}$$

Where  $\gamma^T_s$  is total surface free energy of composite film,  $\gamma^P_s$ ,  $\gamma^D_s$  are polar and dispersive forces of composite polymer, respectively.

$\gamma^P_L$ ,  $\gamma^D_L$  are polar and dispersive forces of standard liquid surface, respectively.

$\theta$  is the contact angle of liquid formed on composite film.

#### 3.1.11 Water solubility

Water solubility of all composite polymer films was determined by a method adapted from Bertan et al. (Bertan et al. 2005: 73-82). The film samples were cut to a square piece of 2.0 x2.0 cm and the cut film was accurately weighed ( $W_0$ ). The films were placed into test beakers with 100 ml distilled water. The samples were dissolved and shaker under constant agitation at 180 rpm for 24 h at 25 °C. The remained pieces of film were, then, filtered by filtration and dried again by hot air oven at 70 °C until a final dried constant weight was obtained ( $W_1$ ). All samples were performed in triplicate. The percentage of solubility was calculated

from the weight difference of filter paper that was dried at 70 °C before and after filtration as equation (Equ. 5):

$$\% \text{ Solubility} = \frac{(W_0 - W_1)}{W_0} \times 100 \dots\dots\dots \text{Equ.5}$$

Where  $W_0$  and  $W_1$  were the accurate dried weight before and after the test, respectively.

### 3.1.12 Water uptake

Water uptake of all composite polymer films was evaluated by a method adapted from Lee et al. (Lee et al. 2004: 251-254). The film samples were cut to a square piece of 2.0 x2.0 cm and the cut film was accurately weighed ( $W_0$ ) which were then dissolved in distilled water for 3 h at 25 °C. The wet samples were then blotted with filtered paper to remove excess liquid and weighed ( $W_1$ ). All samples were performed in triplicate. The equilibrium-swelling in distilled water was calculated according to the following equation (Equ.6):

$$\% \text{ Water uptake} = \frac{(W_1 - W_0)}{W_0} \times 100 \dots\dots\dots \text{Equ.6}$$

Where  $W_0$  and  $W_1$  were the accurate weight of the dried and wet samples, respectively.

### 3.1.13 Moisture content

The composite polymer were accurately weighed ( $W_0$ ) and dried by loss on drying measurement ( $W_1$ ). The weight of films before and after drying was calculated for the moisture content (Equ.7). All samples were performed in triplicate.

$$\text{Moisture content (\%)} = 100(W_0 - W_1)/W_0 \dots\dots\dots \text{Equ.7}$$

Where  $W_0$  and  $W_1$  were the constant weight before and after drying.

### 3.1.14 Moisture sorption isotherm

Moisture sorption isotherm of all composite polymers was evaluated by a method adapted from Sontaya Limmatvapirat et al. (Sontaya Limmatvapirat et al. 2007: 690-698) which was determined by placing composite polymer into a controlled humidity environment at a constant temperature until they were equilibrium. The samples of film were dried by hot air oven at 70 °C for 3 h

until the dried constant weight was obtained. ( $W_0$ ). The dried film samples were then placed in desiccators containing various saturated solutions which gave different relative humidities (RH). The composite polymer was firstly placed into a desiccators containing lithium chloride, the lowest relative humidity, for 5-10 days at 25 °C until the constant weight was obtained ( $W_1$ ). The film sample was then changed from lithium chloride (11.3% RH,  $a_w = 0.113$ ) to the increasing relative humidities in sequential order obtained from other various saturated solutions i.e., magnesium chloride (32.8% RH,  $a_w = 0.328$ ), sodium dichromate (54.4% RH,  $a_w = 0.544$ ), sodium chloride (75.3% RH,  $a_w = 0.753$ ), potassium chloride (84.3% RH,  $a_w = 0.843$ ), potassium nitrate (93.7% RH,  $a_w = 0.937$ ) and distilled water (100.0% RH,  $a_w = 1.00$ ), respectively. The methods were performed as similar to lithium chloride until the constant weight was obtained. A single sample of film was measured five times for each relative humidities ( $n=5$ ). The change in weight constant of composite polymer at various relative humidity was recorded and then the percent moisture content was calculated using the following equation (Equ. 8):

$$\% \text{ Moisture content} = \frac{(W_1 - W_0)}{W_0} \times 100 \dots\dots\dots \text{Equ.8}$$

Where  $W_1$  is the weight of composite polymer when placed in desiccators at various solutions and  $W_0$  is the initial dried weight.

### 3.1.15 Water vapor permeability coefficient

The water vapor permeability coefficient was conducted using modified permeation cell described in the Annual Book of ASTM Standards (ASTM 1989). The cell consisted of a glass bottle, filled with 30 g dried- granular calcium chloride and covered with an opened circular hole of 3-4 cm in area. The film obtained from composite polymer with circular shape was placed inside the cover and then sealed tightly with silicone. The cell was then kept in a cabinet at 40°C and 75%RH. The weight change was recorded every 24 h. The water vapor permeability coefficient (WVPC) of at least five cells for all films was then calculated using the following equation (Equ. 9) :

$$WVPC = (W \times T) / (A \times \Delta P) \dots\dots\dots \text{Equ.9}$$

Where W is the amount of water permeated through the film (g/h), T is the thickness of film (m), A is the area of film (m<sup>2</sup>) and ΔP is the pressure difference. The unit of WVPC is gh<sup>-1</sup>m<sup>-1</sup>Pa<sup>-1</sup>.

### 3.1.16 Mechanical properties

The mechanical properties of the all composite polymer films were evaluated by puncture test as described in Sotaya Limmatvapirat et al. (Sontaya Limmatvapirat et al. 2008: 335-344). A texture analyzer (TA.XT.plus Texture Analyzer, Stable Micro Systems, UK) equipped with a spherical puncturing probe (diameter 5 mm) was employed. The film sample was cut to a square piece of 7 x7 cm. The film was placed in a holder with a cylindrical hole (r = 1.0 cm). The probe was driven through the film with a speed of 0.1 mm/s and force displacement curves were recorded through a 50 N load cell. The maximum load and the maximum displacement of films were measured. The average of five measurements was performed (n=5). The puncture strength and percent elongation were calculated by both equations (Equ. 10-11).

$$\text{Puncture strength} = \frac{F_{\max}}{A_{cs}} \dots\dots\dots \text{Equ.10}$$

Where F<sub>max</sub> is the maximum applied force, A<sub>CS</sub> is the cross-sectional area of the edge of the film located in the path of the cylindrical hole of the film holder, with A<sub>CS</sub> = 2rδ, where r is the radius of the hole and δ is the thickness of the film.

$$\text{Percentage of elongation} = \frac{\sqrt{r^2 + d^2} - r}{r} \times 100 \dots\dots\dots \text{Equ.11}$$

Where r is the radius of the film exposed in the cylindrical hole of the film holder and d represents the displacement of the probe from the point of contact to the point of puncture.

### 3.1.17 Powder X-ray diffraction

The crystallinity of all composite polymers was investigated by the powder X-ray diffractometer (Rigaku, Miniflex, Japan) with Ni-filtered Cu radiation generated in a sealed tube operated at 30 kV and 15 mA. The diffraction curves were obtained from 3 to 26° at a scanning rate of 4° min<sup>-1</sup>. All samples were performed in duplicate.

### **3.2 Stability study of composite polymer based on shellac and gelatin**

The stability study of single shellac and composite polymers varied with the concentrations of gelatin at 10, 20, 30, 40 and 50% w/w and single gelatin were kept in a stability cabinet at 40 °C and 75% RH for 180 days. The stability condition of film was adapted from Manee Luangtana-anan et al. and Sontaya Limmatvapirat et al. (Manee Luangtana-anan et al. 2007 : 687-692 and Sontaya Limmatvapirat et al. 2008: 335-344). The change in physicochemical properties such as, wettability, surface free energy, acid value, insoluble solid, chemical structure, thermal analysis, water content, water vapor permeability coefficient, mechanical properties and powder X-ray diffraction were evaluated. These methods were described in 3.1.

### **3.3 Effect of types and concentrations of plasticizers on mechanical properties, stability of composite polymer based on shellac and gelatin**

In this study, 40% gelatin was appropriate concentration for further investigation for the effect of types and concentrations of plasticizers on the mechanical properties and stability composite polymer film. The composite polymer at 40 % gelatin was prepared as described in 3.1 and then was added with the plasticizers i.e., polyethylene glycol and diethyl phthalate at 5 and 10% w/w. The composite polymer solution with plasticizer was homogenized by magnetic stirrer for about 3 h. The unplasticized and plasticized composite polymer solutions were then poured on a glass plate and were allowed to dry at 50 °C for 8 h. All film samples were kept in a stability chamber at 40 °C and 75% RH for 180 days and also investigated for physicochemical properties such as wettability, surface free energy, water content, water vapor permeability coefficient, mechanical properties, powder X-ray diffraction, chemical structure, acid value and insoluble solid as described in 3.1.

### **3.4 Evaluation of composite polymer with and without plasticizer as edible film coating in food and pharmaceutical applications**

The evaluation of film coating efficiency of composite polymers varied with the concentrations of gelatin at 10, 20, 30, 40 and 50% w/w were predicted by the two parameters, i.e., work of adhesion and spreading coefficient based on the contact angle measurement of known surface free energy of coating liquid over various substrates such as glass surface, Teflon surface, mango skin, banana skin, theophylline tablet and aspirin tablet. Glass and Teflon were applied as model

substrates which represented hydrophilic and hydrophobic model. Mango and banana were both fruits due to the food model substrate while aspirin and theophylline tablet was used indicating the acidic and basic drugs for pharmaceutical application. The contact angle of film coating over model substrates was measured by the sessile drop method using a drop shape instrument FTA 1000 high performance image processing (First Ten Angstroms, USA). All samples were performed in triplicate. The work of adhesion and spreading coefficient was then calculated using the equation as follows (Equ. 12-13):

$$\text{Work of adhesion } (W_a) = \gamma_l(1+\cos\theta) \dots \dots \dots \text{Equ.12}$$

$$\text{Spreading coefficient } (W_s) = \gamma_l(\cos\theta-1) \dots \dots \dots \text{Equ.13}$$

Where  $W_a$  is work of adhesion (mN/m),  $W_s$  is spreading coefficient (mN/m),  $\gamma_l$  is surface free energy of coating solution and  $\theta$  is the contact angle of film coating solution formed on the substrate.

Further study was to investigate the influence of types and concentrations of plasticizers i.e., polyethylene glycol and diethyl phthalate on the film coating efficiency of composite polymers based on 40% gelatin over various substrates with the same the effect of gelatin content.

### **3.5 Application of composite polymer as edible film coating for post harvest quality and prolonged shelf life of banana**

The preparation of banana coating was adapted from Bico et al. (Bico et al. 2009 : 508-514). Bananas cv. Kluai Hom Thong (AAA group) was harvested at 75–80% maturity from a commercial plantation in Nakorn Pathom, Thailand. Hands, free of visual defects and of uniform weight and shape of banana were selected. The fruit was sterilized with 0.1 g /L of sodium hypochlorite solution for 3 min, rinsed and dried. The bananas were first dipped into coating solution i.e., shellac solution (S1), composite solution at 40% gelatin (S2) and composite polymer solution with polyethylene glycol 400 at 5% w/w (S3) for 5 min and dried. The banana coated with S1, S2 and S3 formulations were then compared with uncoated banana (S0). The samples of banana with and without coating were kept in 25 °C and also investigated for their physicochemical properties such as, color, titratable acidity, total soluble sugar (TSS), weight loss and firmness at 0, 3, 7, 10, 15, 20, 25 and 30 days as described in 3.5.1-3.5.5.

### 3.5.1 Color

The color of banana skin was measured by using RGB image program. The banana samples with and without coatings were placed in standard box consisting of light and background and then recorded the images of banana skin. The data was analyzed with histogram of color surface from RGB image program and used in the averages of color to predict the change in color of banana upon storage. The data of color were performed with red (R), green (G) and blue color (B), respectively. Three fruit were used for analysis.

### 3.5.2 Titratable acidity (TA)

Titrateable acidity of all banana samples was evaluated by a method adapted from Bico et al. (Bico et al. 2009 : 508-514). Ten gram of banana from each replicate was crushed and homogenized for 1 hr with 100 ml boiled distilled water. The mixture was titrated with 0.10 N NaOH. The end point was determined by potentiometric titration. The graph between ml of NaOH and pH was plotted and the TA was calculated from the value of midpoint of the sharp change in pH. The titrateable acidity was expressed as milligram of malic acid per 100 g sample (Equ. 14). The average of three measurements was performed.

$$TA = (\text{ml of NaOH} \times 134.09) / (40 \times W) \dots\dots\dots \text{Equ.14}$$

Where W was the accurate weight of banana.

### 3.5.3 Total soluble sugar (TSS)

TSS of banana with and without coating was determined by phenol-sulphuric method according to Bico et al. (Bico et al. 2009 : 508-514). Sugars from banana (0.2 g) were extracted with 10 ml 80% (v/v) ethanol, in a water bath (80-85 °C) for 30 min. The supernatant was collected and the extraction was repeated twice. Ethanol in the supernatant was evaporated in the water bath, and the resulting solution was diluted to 50 ml. A 0.50 ml aliquot of this solution was allowed to react with 0.5 ml of 5% (w/v) phenol solution and 2.5 ml concentrated sulphuric acid. The absorbance was measured at 490 nm after 20 min by spectrophotometer (Shimadzu UV-Vis 1601, Kyoto, Japan) against a reagent blank. The total soluble sugars were calculated using a calibration curve (0.02-0.06 mg /ml). The average of three measurements was performed.

### 3.5.4 Weight loss

Banana with and without coating formulation were accurately weighed ( $W_0$ ) and kept at 25 °C for 30 days. After storage, the samples of banana were accurately weighed ( $W_1$ ) at 0, 3, 7, 10, 15, 20, 25 and 30 days. The average of three measurements was performed. The change in the weight of banana was calculated according to the formula as belows (Equ. 15):

$$\% \text{ Weight loss} = \frac{(W_0 - W_1)}{W_0} \times 100 \dots\dots\dots \text{Equ.15}$$

Where  $W_0$  and  $W_1$  were the accurate dried weight before and after kept at 25 °C, respectively.

### 3.5.5 Firmness

Firmness of banana with and without coating was determined by a texture analyzer (TA.XT.plus Texture Analyzer, Stable Micro Systems, UK) by measuring the force required for a 3 mm cylindrical probe to penetrate 10 mm into the surface at a rate of 5 mm/s. The samples were punctured thrice in each opposite side. A load of 50 N was used. Five fruits were used for the analysis.

## 5. Statistical analyses

Data of research were analyzed as means and standard deviation. The statistical analysis was carried out using analysis of variance at the 0.01 significance level.

## **CHAPTER 4**

### **RESULTS AND DISCUSSION**

#### **1. Physicochemical properties of composite polymer based on shellac and gelatin**

Edible film is widely used in food and pharmaceutical industries and can be prepared from single or combination of biodegradable polymer. The attempt to prepare edible film by the formation of composite polymer between shellac and hydrophilic polymer has been initiated since shellac, as a single film forming, has some drawbacks such as the weak mechanical properties and instability (Manee Luangtana-anan et al. 2007 : 687-692; Sontaya Limmatvapirat et al. 2007 : 690-698; Manee Luangtana-anan et al. 2010 : 12934-12940). Gelatin was chosen as a hydrocolloid polymer for the formation of composite polymer between shellac and gelatin. The composite polymer based on solution and free film was investigated for physicochemical properties such as surface tension, viscosity, pH, acid value, insoluble solid, FTIR spectroscopy, powder X-ray diffraction, thermal analysis, scanning electron microscope (SEM), wettability, surface free energy, water uptake, moisture content, water solubility, moisture sorption isotherm, water vapor permeability and mechanical properties as shown in Table 5-10 and Figure 18-23.

##### **1.1 pH, Surface tension and viscosity**

Table 5 shows the effect of gelatin content on pH, surface tension and viscosity of composite polymer based on solutions. The increase in gelatin content resulted in the decrease in pH of composite polymer solutions and the values were 8.14, 8.02, 7.96, 7.89, 7.81 and 7.79 for different concentrations of gelatin at 0, 10, 20, 30, 40 and 50 % w/w, respectively. This was the result of the positive charge and the lower pH of gelatin (pH = 5.42) contributing to the decrease in pH of all composite polymer solutions. The surface tension of composite polymer increased from 40.55 to 52.12 mN/m when gelatin increased to 50% indicating the increase in hydrophilicity of composite polymer solutions.

In addition, the increase in the surface tension of composite polymer solution was associated with the increase ( $P < 0.01$ ) in viscosity and the values were 0.90, 1.46, 5.04, 14.25, 23.59 MPas for different concentrations of gelatin at 10, 20, 30, 40 and 50 % w/w, respectively. The viscosity of single shellac solution and single gelatin solution was lower than the composite polymer solution and the values were 0.74 and 2.92 MPas, respectively. The higher content of gelatin, the higher viscosity was obtained. The high viscosity was due to the interaction of shellac and gelatin, giving the shellac and gelatin network and hence higher viscosity. The increase in viscosity of composite polymer solution was in agreement with other studies (Sionkowska et al., 2004: 795-801; Gómez-Estaca et al. 2011 : 121-128) which found that the increase in gelatin or collagen content gave the increase in viscosity of composite polymer solution due to the electrostatic interactions between chitosan and gelatin (Gómez-Estaca et al. 2011 : 121-128) or chitosan and collagen (Sionkowska et al. 2004 : 795-801).

Table 5 Effect of gelatin content on surface tension, viscosity and pH of shellac and gelatin composite film solution

<b>Content of gelatin (%w/w)</b>	<b>pH</b>	<b>Surface tension(mN/m)</b>	<b>Viscosity (MPas)</b>
0	8.14 ± 0.06	40.55 ± 0.24	0.74 ± 0.05
10	8.02 ± 0.01	42.70 ± 0.16	0.90 ± 0.08
20	7.96 ± 0.02	44.50 ± 0.28	1.46 ± 0.10
30	7.89 ± 0.03	47.80 ± 0.15	5.04 ± 1.29
40	7.81 ± 0.02	48.36 ± 0.54	14.25 ± 1.52
50	7.79 ± 0.02	52.12 ± 0.64	23.59 ± 3.94
100	5.42 ± 0.04	46.09 ± 1.09	2.92 ± 0.51

### 1.2 Acid value and percentage of insoluble solid

Shellac, a mixture of polyesters and single esters, consists of several hydroxyl groups and carboxyl groups. The amount of carboxyl group was an important group indicating the physicochemical properties of shellac film. It was predicted by the acid value which was expressed as the total number of carboxyl groups per molecule of shellac (Sontaya Limmatvapirat et al. 2004 : 41-49; Manee Luangtana-anan et al. 2007 : 687-692; Sontaya Limmatvapirat et al. 2007 : 690-698). The amount of carboxylic group of shellac in composite polymers with various concentrations of gelatin as displayed in Table 6. It was found that the acid value decreased significantly ( $P < 0.01$ ) as gelatin content increased and the values were 76.00, 70.65, 67.56, 64.43, 62.00 and 57.36 mg KOH/g shellac at the concentrations of 0, 10, 20, 30, 40 and 50%, respectively. The reduction in acid value of shellac proved that there was the interaction between carboxylic groups of shellac and functional group i.e., amino groups of gelatin which might be a result of the electrostatic formation. The addition of gelatin did not cause any change in insoluble solid at all concentrations.

Table 6 Effect of gelatin content on acid value (AV) and insoluble solid (IS) of shellac and gelatin composite polymer film

<b>Content of gelatin (%w/w)</b>	<b>Acid value (mg KOH/g shellac)</b>	<b>IS (%)</b>
0	76.00 ± 0.43	0.74 ± 0.04
10	70.65 ± 2.12	0.64 ± 0.03
20	67.56 ± 3.14	0.50 ± 0.01
30	64.43 ± 1.36	0.56 ± 0.01
40	62.00 ± 0.18	0.44 ± 0.10
50	57.36 ± 0.69	0.67 ± 0.38
100	NA*	0.01 ± 0.00

\* The sample could not measure in this study

### 1.3 Fourier transformed infrared (FTIR) spectroscopy

The chemical structure of shellac and gelatin composite polymers was investigated by Fourier transformed infrared (FTIR) spectroscopy as shown in Figure 18. The FTIR spectrum of shellac (Figure 18a) indicated peaks around  $1716\text{ cm}^{-1}$ ,  $1255\text{ cm}^{-1}$  and  $3430\text{ cm}^{-1}$ , due to the C=O stretching of carboxylic acid, C–O and O–H stretching vibrations, respectively. Since shellac was prepared in ammonium salt ( $\text{NH}_3$ ), the spectra at  $1556$  and  $1385\text{ cm}^{-1}$  were found, indicating the asymmetric and symmetric C=O stretching of carboxylate, respectively. The result was in agreement with a previous study (Sontaya Limmatvapirat et al. 2007 : 690-698). Figure 18g, the FTIR spectrum of gelatin film had the strong peak at  $3200\text{-}3500\text{ cm}^{-1}$  due to N-H stretching,  $1663\text{ cm}^{-1}$  due to C=O and C-N stretching of Amide I,  $1557\text{ cm}^{-1}$  and  $1239\text{ cm}^{-1}$  indicated the N-H bending and C-N stretching of Amide II and Amide III. The characteristic peak of gelatin film was in accordance with other studies (Dong et al. 2006 : 37-44; Andreuccetti et al. 2009 : 1113-1121). The FT-IR spectra of composite polymers with different concentrations of gelatin at 10, 20, 30, 40 and 50% were shown in Figure 18b-18f which indicated the strong absorption band at  $3200\text{-}3500\text{ cm}^{-1}$  due to the O-H broad stretching from shellac and the stretching vibration of N-H group from gelatin. In addition, the result showed the change of peak at  $1716\text{ cm}^{-1}$  due to carbonyl stretching vibration of shellac and at  $1663\text{ cm}^{-1}$  due to the C=O and C-N stretching vibration of gelatin while the change was not reported for the physical mixture of shellac and gelatin at all ratios (Data of physical mixture between shellac and gelatin was shown in Appendix, Figure 52). This change might be the result of the electrostatic interaction between negative charge ( $\text{COO}^-$ ) of shellac and positive charge ( $\text{NH}_3^+$ ) of gelatin. The change in FTIR spectra was correlated with the decrease in the acid value and the increase in viscosity of composite polymer as the gelatin increased and agreed with the other reports (Yu 1999 : 440-444; Xiao et al. 2001 : 1596-1602; Sionkowska et al. 2004: 795-801; Dong et al. 2006 : 37-44; Pranoto et al. 2007 : 766-774; Gómez-Estaca et al. 2011 : 121-128).

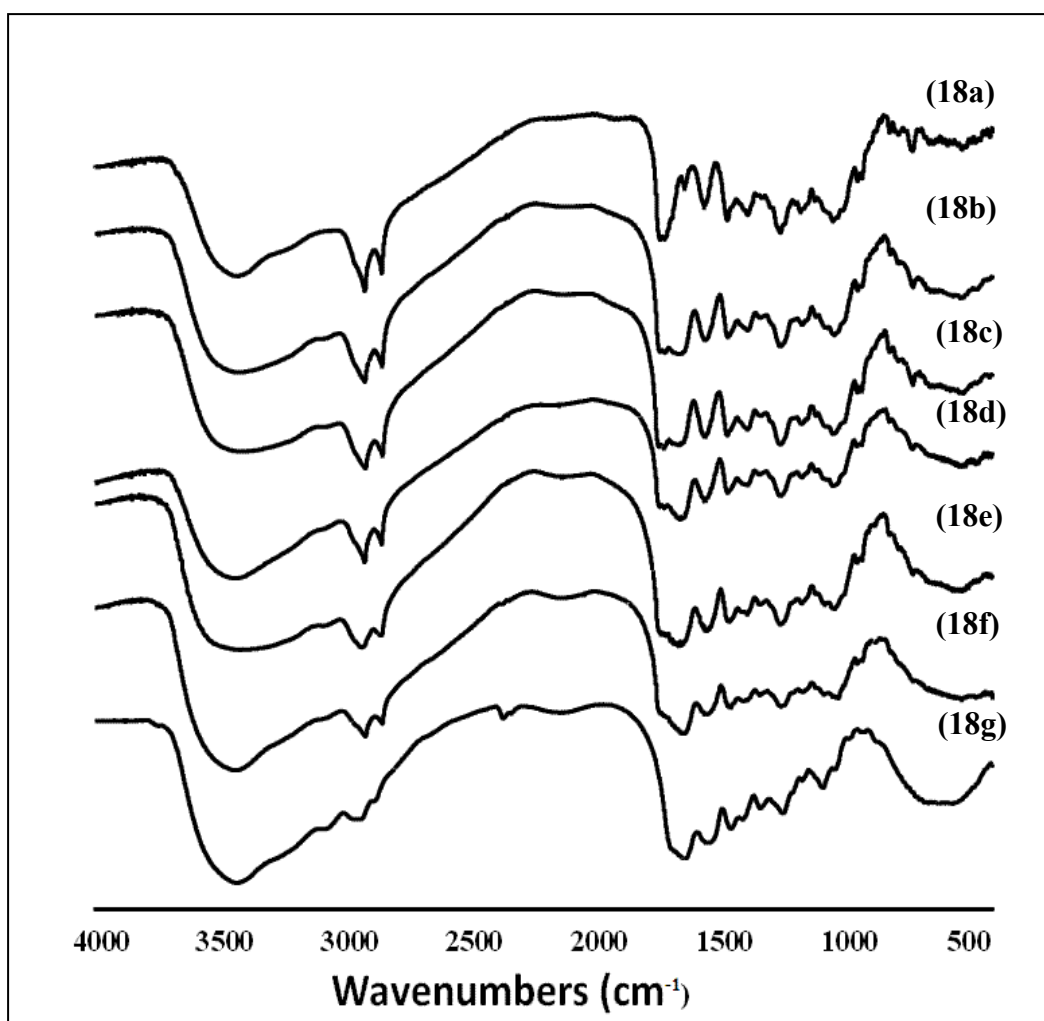


Figure 18 FTIR spectroscopy of shellac (18a), shellac and gelatin composite polymers with various concentrations of gelatin %w/w: 10 (18b), 20 (18c), 30 (18d), 40 (18e), 50(18f) and gelatin (18g)

#### 1.4 Powder X-ray diffraction

Figure 19 shows the PXRD pattern of shellac and gelatin composite polymer films at various concentrations of gelatin. As the increase in gelatin concentrations, the PXRD pattern did not change, indicating that the incorporation of gelatin content did not increase any crystallinity.

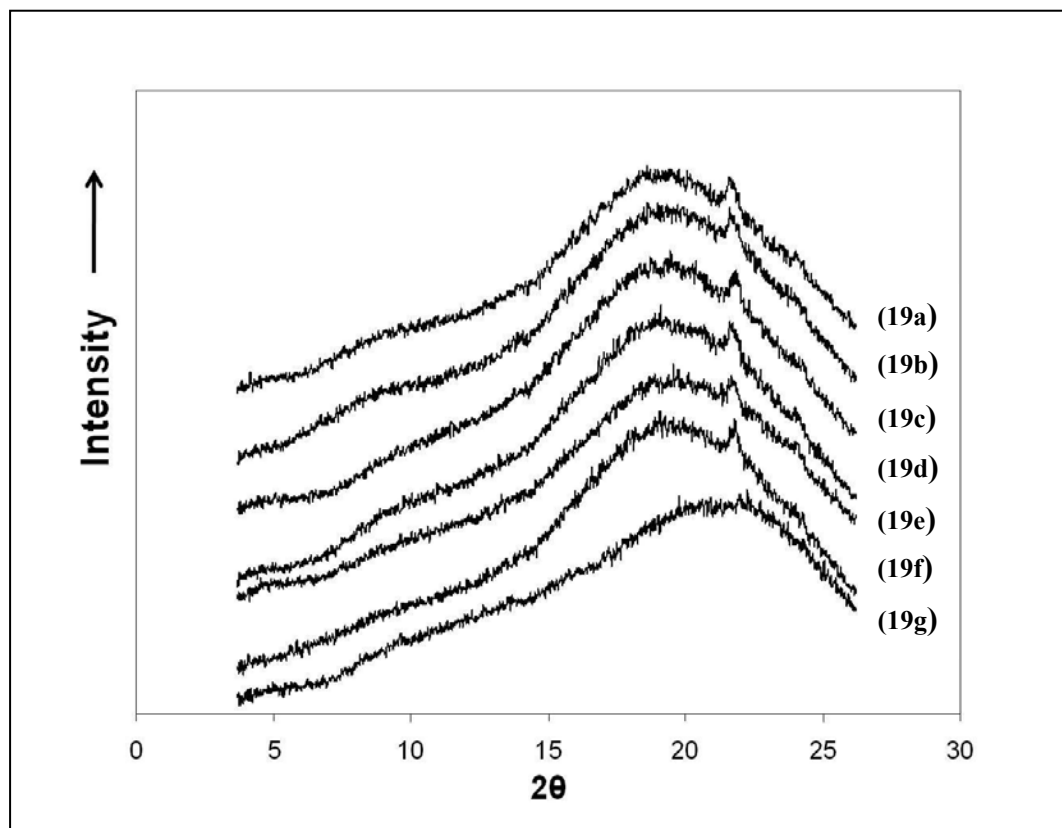


Figure 19 Powder X-ray diffractogram of shellac (19a), shellac and gelatin composite polymers with various concentrations of gelatin %w/w: 10 (19b), 20 (19c), 30 (19d), 40 (19e), 50 (19f) and gelatin (19g)

### 1.5 Thermal analysis

Table 7 shows the effect of gelatin content on thermal behavior of shellac and gelatin composite polymer films varied with the concentrations of gelatin. The result indicated that the higher gelatin content gave the change in the endothermic peak of all polymer films due to the loss of free water causing the increased melting temperature ( $T_m$ ) and enthalpy of polymer films. (The characteristic of peak was shown in appendix, Figure 50-51) The melting temperatures of all polymer films were in the range of 50-100 °C and the peak of  $T_m$  were 76.12, 76.83, 77.05, 79.16, 83.52, 86.48 and 99.1 °C for shellac film, composite polymers varied with the amount of gelatin at 10, 20, 30, 40 and 50% and gelatin film, respectively. The change in the endothermic peak of all composite polymer films was due to the loss of free water and increased from 0.62 to 4.25% when the amount of gelatin in the blend increased to

50%, attributing to the change in the enthalpy of composite polymer film. The enthalpy values ( $\Delta H$ ) of composite polymer films were increased from 67.5 to 118.12 J/g as the gelatin increased to 50%. The higher gelatin content exhibited the higher water caption, causing the higher free water content of composite polymer films which was correlated with the previous reports when gelatin was added in other polymers, i.e., chitosan, gellan and soy protein (Cheng et al. 2003: 2871-2880; Lee et al. 2004: 251-254; Cao et al. 2007: 1153-1162).

Table 7 Effect of gelatin content on maximum of endothermic peak, enthalpy and percent water loss of shellac and gelatin composite polymer films

<b>Content of gelatin (%w/w)</b>	<b>Peak temperature (<math>^{\circ}\text{C}</math>)</b>	<b>Enthalpy (J/g)</b>	<b>Water loss (%)</b>
0	76.12	67.50	0.62
10	76.83	77.65	1.08
20	77.05	91.20	2.50
30	79.16	104.73	2.69
40	83.52	115.80	4.12
50	86.48	118.12	4.25
100	99.10	120.18	4.76

### 1.6 Morphology

Figure 20 shows the SEM micrograph of film surface and film cross section obtained from shellac, composite polymers with different concentrations of gelatin (10, 20, 30, 40 and 50%) and gelatin. The result demonstrated that the morphology of film surface and film cross section did not change as the incorporation of gelatin within the shellac network of all concentrations, indicated by the smoothness and homogeneous of the surface and cross section of all films

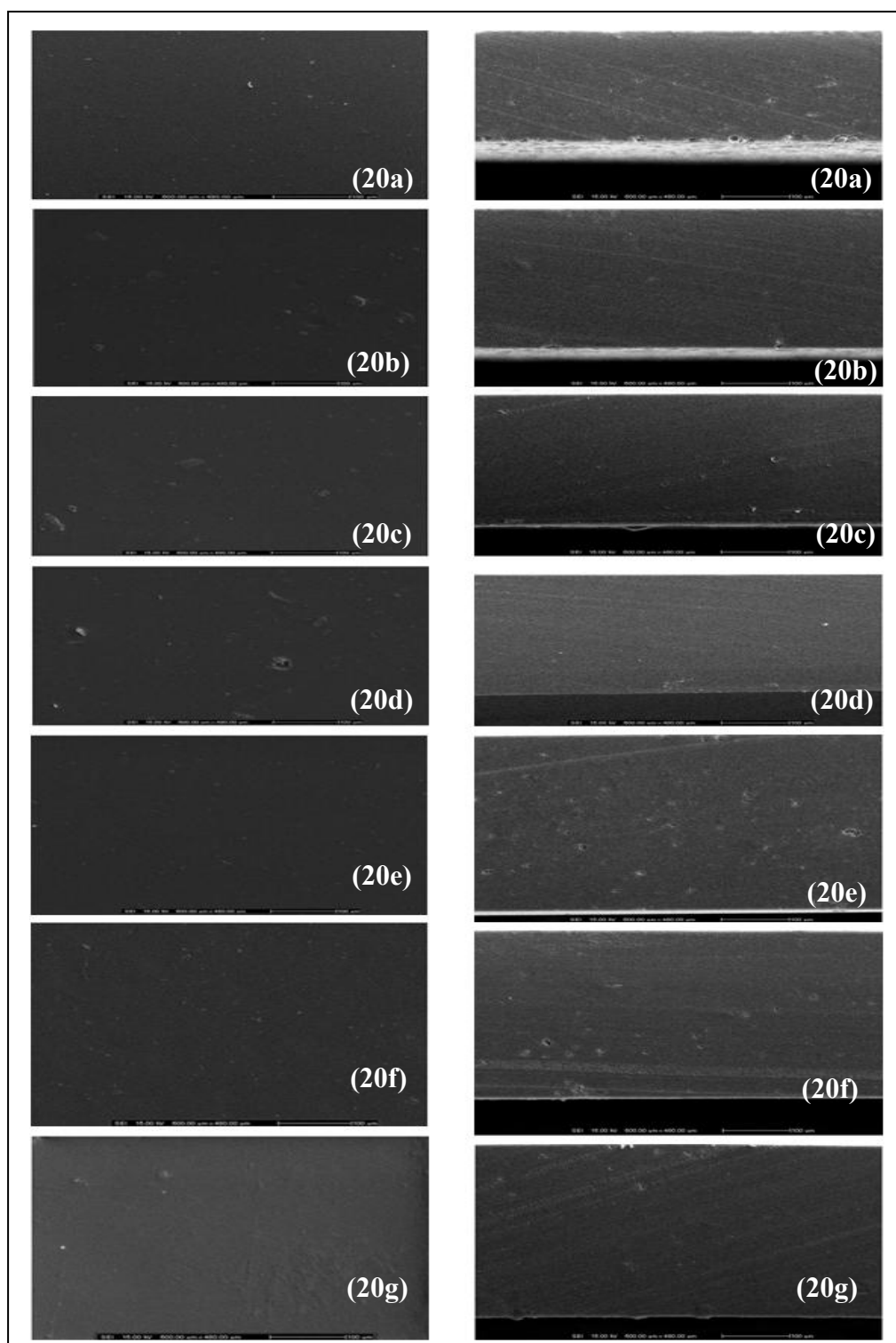


Figure 20 SEM micrograph of film surface (left) and cross section (right) of single shellac film (20a), composite polymer films with various concentrations of gelatin %w/w: 10 (20b), 20 (20c), 30 (20d), 40 (20e), 50 (20f) and single gelatin film (20g)

### 1.7 Wettability and surface free energy

Table 8 shows the effect of gelatin content on wettability of shellac and gelatin composite polymer films. The higher wettability was observed as the increase in gelatin concentrations indicated by the lower contact angle when water was used as wetting liquid. The contact angle was an indicator of the wettability and hydrophilicity of films (Su et al. 2010 : 145-153). The degree of contact angle decreased significantly ( $P < 0.01$ ) from 81.39 to 68.55<sup>0</sup> when gelatin increased to 50%. The result was in agreement with previous reports for chitosan-soy protein (Silva et al. 2007 : 25-31) and chitosan-gelatin blended films (Cheng et al. 2003 : 2871-2880). Silva et al. indicated that the higher protein content, the lower contact angle was obtained, resulting from the increase in hydrophilicity and wettability of composite polymer film (Silva et al. 2007 : 25-31). Cheng et al. reported the change in wettability of chitosan when gelatin was added. The contact angles for all the materials were less than 70<sup>0</sup>, indicating that all these materials had a good wettability and proving their hydrophilicity (Cheng et al. 2003 : 2871-2880). However, the opposite results were obtained when diiodomethane was applied as the non polarity wetting liquid and was in agreement with Rotta et al. The contact angle increased significantly ( $P < 0.01$ ) from 62.87 to 73.10 degree when gelatin was added up to 50% (Rotta et al. 2009 : 619-623). The increase in wettability was complied with the higher total surface free energy, the lower dispersive force and the higher polarity force as the increase in gelatin.

Table 9 shows the effect of gelatin content on the surface free energy of shellac and gelatin composite polymer films. The surface free energy ( $\gamma^T_s$ ) of composite polymer film is determined by Wu harmonic equation and consisted of polar and dispersive forces. The total surface free energy ( $\gamma^T_s$ ) of shellac was lower than that of composite polymer which increased significantly ( $P < 0.01$ ) from 37.28 to 43.30 mN/m when gelatin increased to 50% w/w. The percent polarity also increased from 26.23% to 42.82%, indicating the higher hydrophilicity as the increase in the gelatin content. The total surface free energy proved to be dependent on the concentration of gelatin in composite polymer. The result was in agreement with other works (Silva et al. 2007 : 25-31; Rotta et al. 2009 : 619-623) when the second

hydrophilic polymer was added. Rotta et al. showed that the surface free energy of chitosan/HPMC blended film increased from 37.4 to 41.30 mN/m when HPMC increased to 70% (Rotta et al. 2009 : 619-623). Silva et al. found that the higher soy protein content gave the decreased dispersive force ( $\gamma^D_s$ ) from 27.4 to 19.4 mN/m and increased polar force ( $\gamma^P_s$ ) from 0.4 to 14.5 mN/m when soy protein was added, resulting in the increased total surface free energy ( $\gamma^T_s$ ) of chitosan and soy protein blended film (Silva et al. 2007 : 25-31). Therefore, it could be concluded that the presence of gelatin contributed to the increase in hydrophilicity of composite polymer.

Table 8 Effect of gelatin content on wettability of shellac and gelatin composite polymer films

Content of gelatin (%w/w)	Contact angle (degree)		
	Water	Formamide	Diiodomethane
0	81.39 ± 1.32	57.72 ± 0.68	62.87 ± 1.96
10	78.15 ± 1.29	53.68 ± 2.04	63.70 ± 1.01
20	75.91 ± 2.04	51.73 ± 1.32	64.97 ± 2.56
30	73.97 ± 1.10	49.35 ± 0.60	68.74 ± 1.02
40	70.89 ± 0.72	48.95 ± 1.08	71.30 ± 5.28
50	68.55 ± 0.57	45.48 ± 1.32	73.10 ± 1.29
100	64.12 ± 3.40	38.23 ± 2.70	75.06 ± 2.89

Table 9 Effect of gelatin content on surface free energy, their component and percent polarity of shellac and gelatin composite polymer films

Content of gelatin (%w/w)	Surface free energy and their component			
	Total (mN/m)	Dispersive (mN/m)	Polar (mN/m)	Polarity (%)
0	37.28 ± 1.96	27.50 ± 2.49	9.78 ± 2.67	26.23
10	39.10 ± 1.01	27.61 ± 1.87	11.49 ± 2.90	29.39
20	40.00 ± 2.56	27.25 ± 1.45	12.75 ± 1.06	31.88
30	40.83 ± 1.02	26.27 ± 1.99	14.56 ± 1.56	35.66
40	41.46 ± 1.28	24.94 ± 2.56	16.52 ± 2.54	39.85
50	43.30 ± 1.29	24.76 ± 2.09	18.54 ± 3.98	42.82
100	47.24 ± 1.87	26.22 ± 1.80	21.03 ± 2.58	44.50

### 1.8 Moisture content, water uptake, water solubility, moisture sorption isotherm and water vapor permeability coefficient

The sensitivity to water of edible films was the most important parameter requirements in food and pharmaceutical applications which was expressed in term of water uptake, moisture content, water solubility, moisture sorption isotherm and water vapor permeability coefficient as shown in Table 10 and Figure 21. The increase in moisture content and water uptake attributed to the higher water solubility and was in accordance with the increase in wettability and surface free energy. The water solubility increased significantly ( $P < 0.01$ ) with the higher proportions of gelatin and the values were 9.89, 14.24, 22.70, 37.36, 43.64 and 54.24% for different concentrations of gelatin at 0, 10, 20, 30, 40 and 50% w/w, respectively. The increase in all water parameters was a result of high polarity of composite polymers, which could attract the higher amount of water and was in accordance with Pinottia et al. (Pinotti et al. 2007 : 66-72). They found that the higher concentrations of methylcellulose in composite polymer based on chitosan and methylcellulose gave the higher hydrophilicity, leading to the increase in water solubility of film. The water uptakes were 80.83, 149.87, 282.73, 316.93, 368.49 and 421.27 % for different concentrations of gelatin at 0, 10, 20, 30, 40 and 50 % w/w, respectively. The increase

in water uptake of film was in agreement with Cao et al. (Cao et al. 2007 : 1153-1162).

The higher water uptake as the increase in gelatin content might be due to the higher extent of swelling of gelatin compared with shellac and was related to the moisture sorption isotherm as indicated in Figure 21. The moisture sorption isotherm used to describe the relationship between moisture content and water activity of biological material (Yang and Paulson 2000 : 571-578). As the higher gelatin content, the higher percent moisture sorption was observed, resulting in the enhancement of hygroscopic film. The percent moisture sorption isotherm at 100% relative humidity ( $a_w = 1.00$ ) increased significantly ( $P < 0.01$ ) from 33.34% to 79.13% when gelatin added up to 50% w/w. The increase in moisture sorption isotherm was due to the reorganization of the polymer network, with the consequent increase in free volume.

Table 10 Effect of gelatin content on moisture content, water solubility, water uptake and water vapor permeability of shellac and gelatin composite polymer films

Content of gelatin (%w/w)	Parameter			
	Moisture content (%)	Water solubility (%)	Water uptake (%)	WVPC x 10 <sup>-8</sup> (gh <sup>-1</sup> m <sup>-1</sup> Pa <sup>-1</sup> )
0	8.61 ± 1.00	9.89 ± 2.49	80.83 ± 6.33	4.15 ± 0.16
10	9.56 ± 0.23	14.24±1.79	149.87 ± 27.36	4.43 ± 0.61
20	10.10 ± 0.71	22.70± 2.17	282.73 ± 19.53	4.92 ± 0.19
30	10.62 ± 0.52	37.36± 4.24	316.93 ± 27.34	5.34 ± 0.51
40	12.46 ± 0.28	43.64± 3.71	368.49 ± 39.98	6.12 ± 0.80
50	12.74 ± 1.63	54.24± 2.10	421.27 ± 42.66	9.46 ± 0.46
100	14.54 ± 2.89	100.0 ± 0.00	NA*	12.15 ± 2.90

\* Film was dissolved in water at 3 hr.

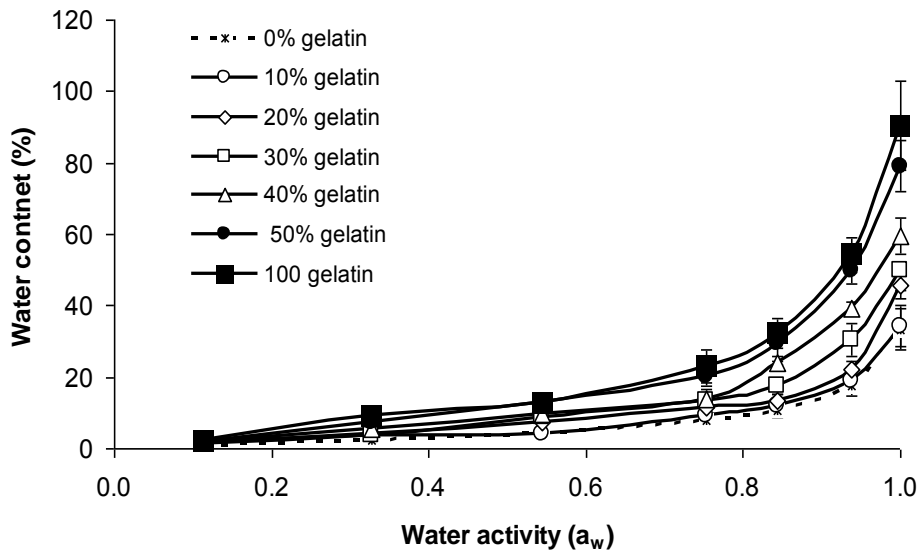


Figure 21 Effect of various concentrations of gelatin on moisture sorption of shellac and gelatin composite polymers

The increase in moisture sorption isotherm led to the increase in water vapor permeability coefficient (WVPC) of films significantly ( $P < 0.01$ ) with the higher incorporation of gelatin and the coefficient values were  $4.15 \times 10^{-8}$ ,  $4.43 \times 10^{-8}$ ,  $4.92 \times 10^{-8}$ ,  $5.34 \times 10^{-8}$ ,  $6.12 \times 10^{-8}$  and  $9.46 \times 10^{-8} \text{ gh}^{-1}\text{m}^{-1}\text{Pa}^{-1}$  for different concentrations of gelatin at 0, 10, 20, 30, 40 and 50% w/w, respectively as shown in Figure 28. Generally, the water vapor permeability of natural polymer film was dependent on both diffusivity and the water solubility of the film (Yang and Paulson 2000 : 571-578). As the higher gelatin, the higher solubility was obtained, resulting in the promotion of water vapor diffusivity and the increase in the water vapor permeability coefficient of films. This proved that the structure of shellac film was more rigid and compact than that of composite polymer films. The increase in WVPC was in agreement with other reports (Yildirim 1998 : 248-252; Gounga et al. 2007 : 521-530; Ferreira et al. 2009 : 807-813; Su et al. 2010 : 145-153). Ferreira et al. (Ferreira et al. 2009 : 807-813) and Gounga et al. (Gounga et al. 2007 : 521-530) found that the higher protein content gave the higher water vapor permeability of film, attributing to the enhancement of hydrophilicity of film. Yildirim and Hettiarachchy (Yildirim 1998 : 248-252) and Su et al. (Su et al. 2010 : 145-153) reported that the

increase in WVPC value of composite film was due to the increase in mobility of polymer chains, reflecting the increase in elongation. The increase in chain mobility attributed to the increase in the water diffusion coefficient and greater water vapor permeability. However, the increase in WVPC of composite polymer films at different concentrations of gelatin was still in a low level when compared to single shellac and other synthetic enteric polymer i.e., cellulose acetate phthalate and hydroxypropyl methylcellulose phthalate (Sontaya Limmatvapirat et al. 2008 : 335-344).

### **1.9 Mechanical properties**

The mechanical properties of composite polymer films varied with the proportions of gelatin were performed by texture analyzer and were measured in terms of puncture strength and percentage of elongation as displayed in Figure 22. The puncture strength increased significantly ( $P < 0.01$ ) with the increase in gelatin content and was in agreement with other reports (Chambi and Grosso 2006 : 458-466; Dong et al. 2006 : 37-44; Cao et al. 2007 : 1153-1162). Cao et al. found that the tensile strength of gelatin and soy protein composite films increased with the increase in gelatin content (Cao et al. 2007 : 1153-1162). Dong et al. demonstrated that the mechanical strength of alginate and gelatin composite film increased from 67 to 100 MPa when gelatin was added to 50% w/w (Dong et al. 2006 : 37-44). Chambi and Grosso reported that the higher gelatin content, the higher tensile strength was achieved, leading to the enhancement of mechanical strength of casein film (Chambi and Grosso 2006 : 458-466). The incorporation of gelatin within shellac network was attributed to the electrostatic interaction, leading to the increase in the puncture strength as shown in the structure diagram in Figure 23. The increase in puncture strength supported the electrostatic formation and agreed with FTIR spectroscopy and other studies when second polymer was added giving the stronger film (Xiao et al. 2001 : 1596-1602; Xu et al. 2005 : 185-192; Dong et al. 2006 : 37-44; Pranoto et al. 2007 : 766-774). The percentage of elongation increased significantly ( $P < 0.01$ ) when the high proportion of gelatin was added and was in agreement with Qussi and Suess (Qussi and Suess 2006 : 403-412). They reported the higher percent elongation of shellac film as the incorporation of hydrophilic polymer such as hydroxypropyl

methylcellulose, methyl cellulose and carbomer. At 50% w/w gelatin showed the highest percent elongation of film and the value was 32.47 %. The higher percent elongation might be the result of the higher caption of water by higher gelatin content indicated by the higher percent water content and the percent polarity of composite polymer films as gelatin increased to 50% w/w. The result was in accordance with the study of Cheng et al. which found that the higher gelatin content, the higher water content was obtained, leading to the increase in the percentage of elongation of chitosan film (Cheng et al. 2003 : 2871-2880). In addition, the water could act as plasticizer (Wu 1982 : 240-243) as reported in many studies (Lee et al. 2004 : 251-254; Cao et al. 2007 : 1153-1162) and the higher elongation and homogeneous of film was obtained as the increase in gelatin content.

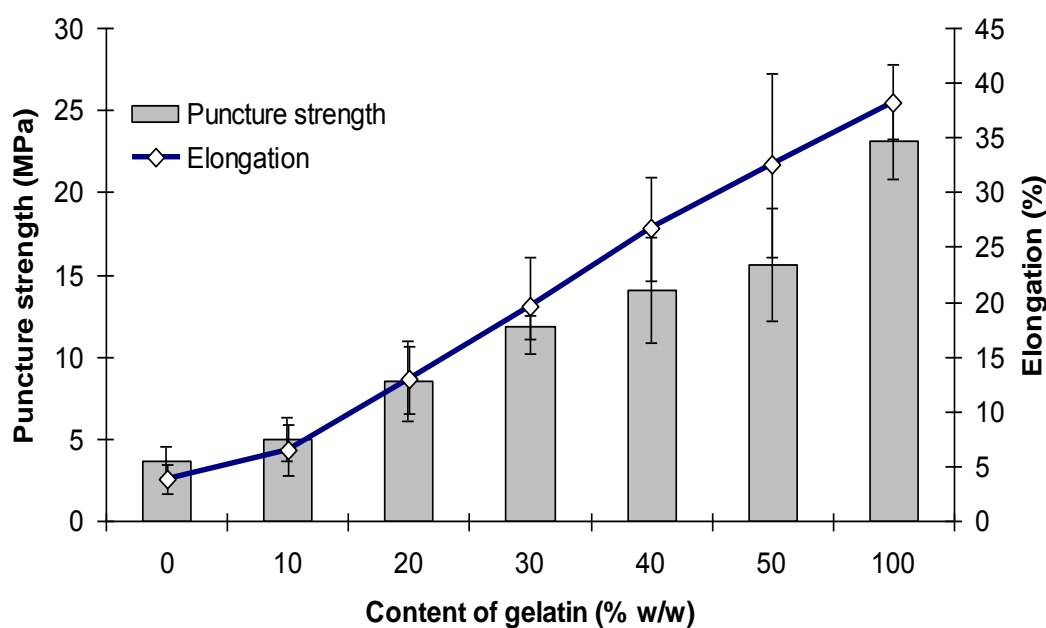


Figure 22 Effect of gelatin content on mechanical properties of shellac and gelatin composite polymer films

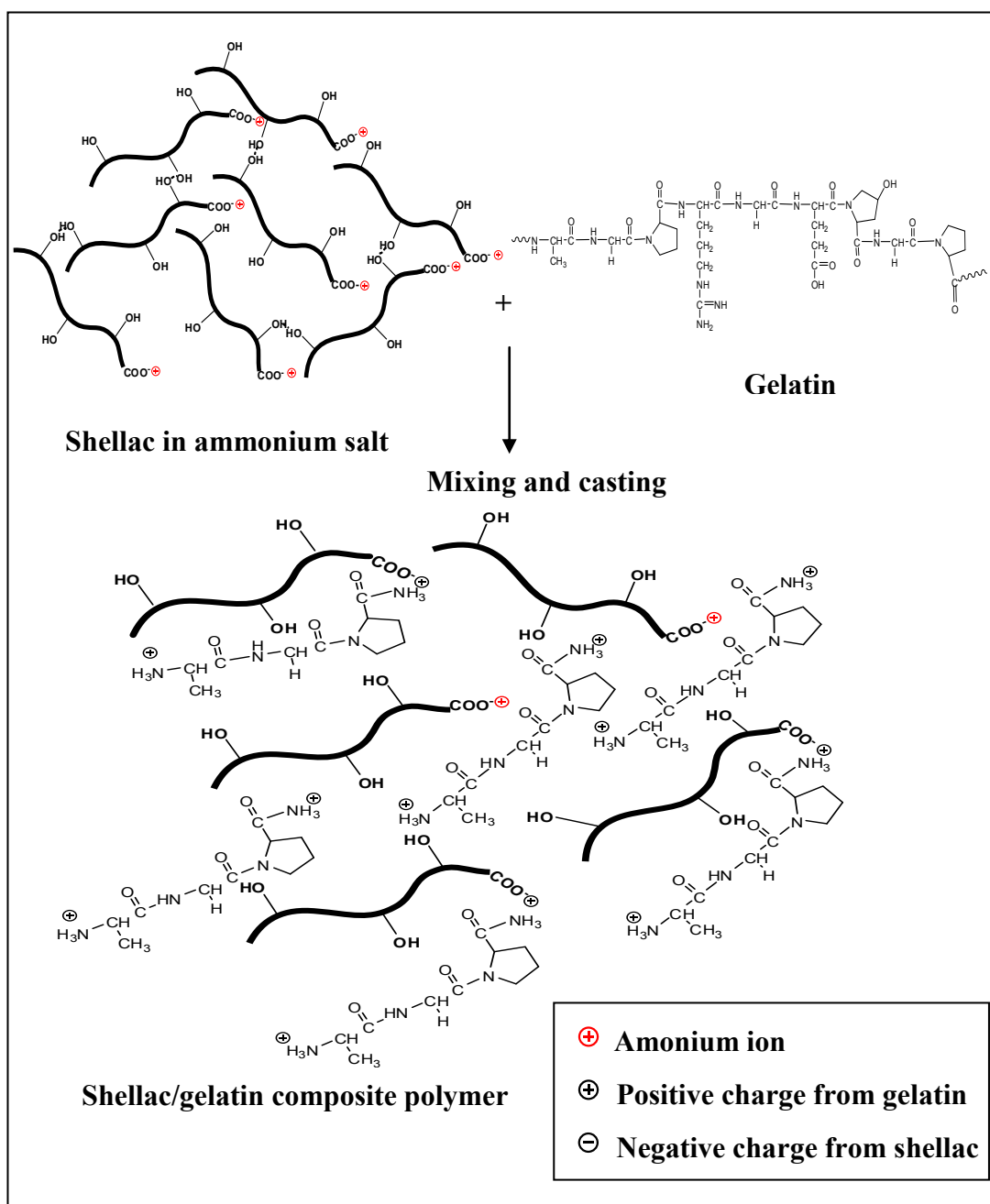


Figure 23 Electrostatic interaction diagram of composite polymer based on shellac and gelatin

### **1.10 Summary**

From the result could be concluded that the formation of composite polymer based on shellac and gelatin could be formed by the electrostatic interaction between negative charge ( $\text{COO}^-$ ) from shellac and positive charge ( $\text{NH}_3^+$ ) from gelatin. The addition of gelatin exhibited the higher wettability, surface free energy and percent polarity as the increase in gelatin content, indicating the increase in hydrophilicity. The higher hydrophilicity attributed to the increase in water solubility, moisture content, water uptake, moisture sorption isotherm, water vapor permeability coefficient and mechanical properties. Further study was performed to investigate the stability of composite polymer at  $40\text{ }^\circ\text{C}$  75 % RH upon storage for 180 days as displayed in topic 2.

### **2. Stability study of composite polymer based on shellac and gelatin**

Shellac, a mixture of polyesters and single esters, comprises of hydroxyl groups and carboxyl groups. The aging of shellac was a result of the polymerization among these groups, causing the instability (Luce 1978 : 51-55; Sontaya Limmatvapirat et al. 2008 : 335-344). It had affect the changes on the various properties such as wettability, surface free energy, acid value, insoluble solid, FTIR spectroscopy, mechanical properties, water vapor permeability coefficient, powder X-ray diffraction and thermal analysis. Therefore, these parameters were used to predict the stability of shellac film. From previous study, the stability of shellac could be improved by the preparation of shellac in ammonium salt form due to the protection of ammonium ion at the carboxylic site of shellac group, resulting in less polymerization. However, shellac in ammonium salt form could protect the stabilization only 90 days of storage and further storage gave the increase in the percent insoluble solid and the reduction of the acid value, attributing to the instability. The result was due to the loss of ammonium ion after storage at  $40\text{ }^\circ\text{C}$ , 75% RH (Manee Luangtana-anan et al. 2007 : 687-692; Sontaya Limmatvapirat et al. 2007 : 690-698). An approach to improve the drawback of shellac was prepared by the formation of composite polymer with hydrophilic polymer. Gelatin was chosen as a hydrophilic polymer to the formation of composite polymer film between shellac

and gelatin and was investigated for their physicochemical properties and stability upon storage for 180 days at 75% RH, 40 °C as shown in Table 11-16 and Figure 24-34.

### **2.1 Wettability and surface free energy**

Table 11 shows the effect of storage time on the wettability of composite polymer films varied with the concentrations of gelatin. Upon storage for 180 days, all film samples tended to decrease the wettability of film, indicating by the increase in the contact angle of polymer films at all the concentrations of gelatin when water was used as wetting liquid. The contact angle of shellac (0% gelatin) increased from 81.39 to 83.34 and 92.01 degrees while at 50% gelatin was changed from 68.55 to 73.69 and 75.09 degrees after storage for 90 and 180 days, respectively. Similar result was obtained for other concentrations of gelatin in the composite polymer films.

Table 12-14 shows the effect of storage times on the surface free energy and their components of composite polymer films varying with the amount of gelatin. After storage for 180 days, all film samples tended to show the reduction in hydrophilicity indicating by the increase in dispersive force and decrease in surface free energy and polar force. The surface free energy of shellac (0% gelatin) decreased from 37.28 to 34.96 and 34.32 mN/m while at 50% gelatin was changed from 43.30 to 40.26 and 40.04 mN/m after storage for 90 and 180 days, respectively. The reduction in hydrophilicity upon storage was reported for all composite polymer films. The change in surface free energy was in agreement with the change in wettability. In addition, the reduction in hydrophilicity could be explained by the reduction in percent polarity as shown in Table 15. Upon storage for 180 days, the percent polarity tended to decrease at all composite polymer films varying with the gelatin content. The change was significant ( $P < 0.01$ ). The percent polarity decreased from 26.23%, 29.39%, 31.88%, 35.66%, 39.85% and 42.82 % to 14.98 %, 24.11 %, 24.95 %, 26.42%, 28.17% and 27.52 % at the proportions of 0, 10, 20, 30, 40 and 50% gelatin, respectively after 180 days of storage.

Table 11 Effect of gelatin content on contact angle of shellac and gelatin composite polymer films upon storage at 40 °C, 75% RH for 180 days when water was used as standard liquid

Content of gelatin (% w/w)	Contact angle (degree)		
	day 0	day 90	day 180
0	81.39 ± 1.32	83.34 ± 3.30	92.01 ± 1.18
10	78.15 ± 1.29	80.35 ± 2.64	84.59 ± 2.35
20	75.91 ± 2.04	79.23 ± 2.33	80.83 ± 1.37
30	73.97 ± 1.10	77.01 ± 1.57	79.19 ± 0.24
40	70.89 ± 0.72	75.61 ± 0.89	76.50 ± 1.20
50	68.55 ± 0.57	73.69 ± 3.33	75.09 ± 4.11

Table 12 Effect of gelatin content on surface free energy of shellac and gelatin composite polymer films upon storage at 40 °C, 75% RH for 180 days

Content of gelatin (% w/w)	Total Surface free energy ( $\gamma^T_s$ , mN/m)		
	day 0	day 90	day 180
0	37.28 ± 1.96	34.96 ± 3.96	34.32 ± 4.05
10	39.10 ± 1.01	37.47 ± 3.57	37.33 ± 4.51
20	40.00 ± 2.56	38.56 ± 3.33	38.07 ± 3.97
30	40.83 ± 1.02	39.49 ± 2.74	38.53 ± 4.01
40	41.46 ± 1.28	39.61 ± 2.79	38.84 ± 3.37
50	43.30 ± 1.29	40.26 ± 3.72	40.04 ± 3.83

Table 13 Effect of gelatin content on dispersive force of shellac and gelatin composite polymer films upon storage at 40 °C, 75% RH for 180 days

Content of gelatin (% w/w)	Dispersive force ( $\gamma^D_s$ , mN/m)		
	day 0	day 90	day 180
0	27.50 ± 2.49	25.99 ± 5.72	29.18 ± 2.67
10	27.61 ± 1.87	27.98 ± 3.62	28.33 ± 1.88
20	27.25 ± 1.45	28.22 ± 4.53	28.57 ± 5.57
30	26.27 ± 1.99	28.97 ± 3.68	28.35 ± 2.56
40	24.94 ± 2.56	27.89 ± 3.73	27.90 ± 1.67
50	24.76 ± 2.09	28.04 ± 5.60	29.02 ± 1.90

Table 14 Effect of gelatin content on polar force of shellac and gelatin composite polymer films upon storage at 40 °C, 75% RH for 180 days

Content of gelatin (% w/w)	Polar force ( $\gamma^P_s$ , mN/m)		
	day 0	day 90	day 180
0	9.78 ± 2.67	8.97 ± 2.05	5.14 ± 1.28
10	11.49 ± 2.90	9.49 ± 2.31	9.00 ± 2.14
20	12.75 ± 1.06	10.34 ± 1.48	9.50 ± 2.67
30	14.56 ± 1.56	11.52 ± 1.04	10.18 ± 1.21
40	16.52 ± 2.54	11.72 ± 1.56	10.94 ± 2.34
50	18.54 ± 3.98	12.22 ± 3.16	11.02 ± 1.78

Table 15 Polarity of shellac and gelatin composite polymer film upon storage for 180 days at 40 °C, 75 % RH

Content of gelatin (% w/w)	Polarity (%)		
	day 0	day 90	day 180
0	26.23 ± 5.33	25.66 ± 3.52	14.98 ± 5.86
10	29.39 ± 3.47	25.33 ± 6.89	24.11 ± 4.21
20	31.88 ± 2.84	26.82 ± 5.98	24.95 ± 4.50
30	35.66 ± 0.11	29.17 ± 6.06	26.42 ± 5.50
40	39.85 ± 4.77	29.59 ± 4.55	28.17 ± 5.09
50	42.82 ± 2.34	30.35 ± 7.01	27.52 ± 4.00

## 2.2 Acid value and percentage of insoluble solid

The acid value and percentage of insoluble solid were both indicators to predict the stability of shellac, due to the structure of shellac mostly consisted of hydroxyl groups and carboxyl groups. Therefore, the acid value could evaluate the amount of carboxyl groups per molecule of shellac (Manee Luangtana-anan et al. 2007 : 687-692; Sontaya Limmatvapirat et al. 2007 : 690-698). Figure 24 shows the effect of storage time on the acid value of composite polymers varying with the proportions of gelatin. The decrease in the acid value attributed to the reduction in carboxyl groups of shellac as a result of the electrostatic interaction between shellac and gelatin. Upon storage, the acid value of single shellac and shellac incorporation with the lower concentrations of gelatin extremely decreased whereas the incorporation of gelatin at the higher concentrations (30%, 40% and 50%) within shellac molecule showed the slightly decreased the acid value after 180 days of storage, exhibiting the higher stability of shellac. The acid value of shellac and at low concentration of gelatin (20%) decreased from 76.00 to 58.73 mg KOH / g shellac and from 67.56 to 54.90 mg KOH / g shellac after 180 days of storage, respectively.

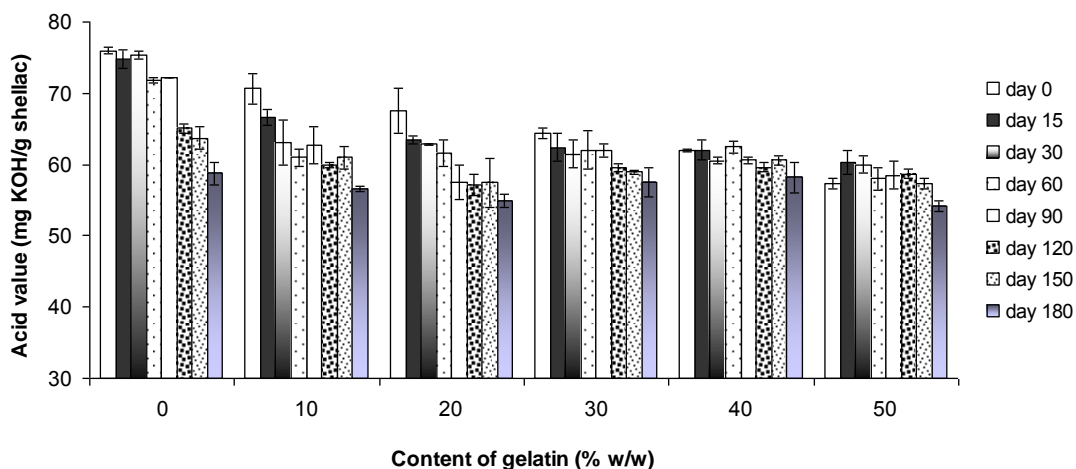


Figure 24 Effect of gelatin content on the acid value of shellac and gelatin composite polymer films upon storage at 40 °C and 75% RH for 180 days

The reduction of acid value was related with the increase in the percentage of insoluble solid as shown in Figure 25. The insoluble solid (IS) increased from 0.74, 0.64, 0.50, 0.56, 0.44 and 0.67 % to 51.69 %, 45.28 %, 23.83 %, 6.02, 1.61 and 1.55 % at the concentrations of 0, 10, 20, 30, 40 and 50%, respectively after 180 days of storage. The statistically significant change ( $P < 0.01$ ) in percent insoluble solid was shown for the single shellac and shellac incorporation with the low concentrations of gelatin (10% and 20%) whereas the low insoluble solid was reported for shellac incorporation with the high concentrations of gelatin (30%, 40% and 50%) upon 180 days of storage.

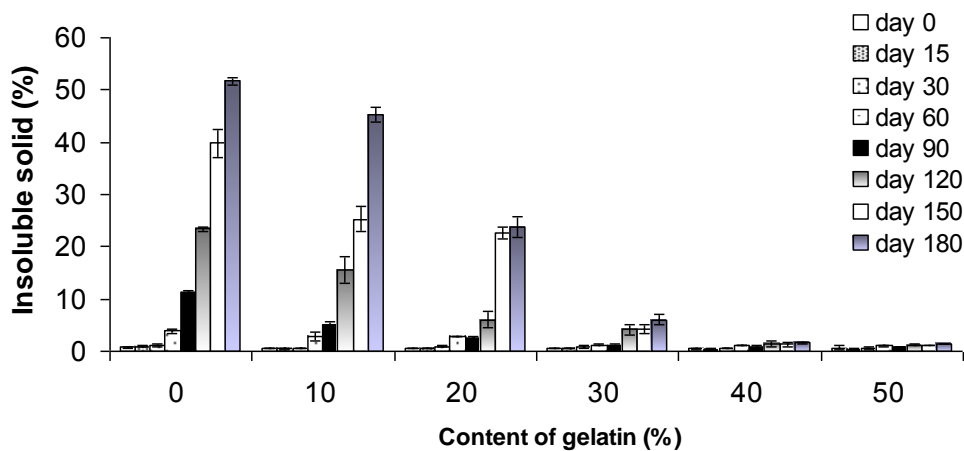


Figure 25 Effect of gelatin content on percentage of insoluble solid of shellac and gelatin composite polymer films upon storage at 40 °C and 75% RH for 180 days

### 2.3 Fourier transformed infrared (FTIR) spectroscopy

Effect of storage times on the chemical structure of single shellac film, single gelatin film and composite polymer films varied with the proportions of gelatin as shown in Figure 26. The result indicated that the spectra of shellac in ammonium salt form at  $1556\text{ cm}^{-1}$  was decreased upon storage for 90 days, resulting from the loss of ammonium ion. This result was attributed to the protection of polymerization only 90 days of storage and further storage gave the increase in the instability. The change in FTIR spectra of shellac in ammonium salt form was related with the decrease in the acid value and the extreme increase in the percentage of insoluble solid whereas the FTIR spectra of single gelatin did not change of all storage for 180 days suggesting that the good stability and correlated with the lower percent insoluble solid. (The insoluble solid of gelatin was shown in appendix, Table 35) The FTIR spectra of composite polymer films varied with ratio of gelatin indicated the changed of peak in the overlap region between shellac and gelatin at  $1663\text{ cm}^{-1}$  and  $1716\text{ cm}^{-1}$  as shellac incorporation with the low concentrations of gelatin (10 % and 20%) upon storage for 90 and 180 days, respectively. The result was due to the reduction of electrostatic interaction between shellac and gelatin, leading to the increase in the polymerization process at these function groups of films, causing the instability. The incorporation of

gelatin at 30% within the shellac network showed the slight change of peak while the higher concentrations of gelatin (40% and 50%) did not change the spectra of composite polymer films upon storage for 180 days and was related with the lower change in acid value and the percentage of insoluble solid. Therefore, the result concluded that the low concentration of gelatin (10% and 20%) could not prevent the polymerization among these groups of shellac whereas the high concentration of gelatin (30%, 40% and 50%) could protect the polymerization of shellac. The result was owing to the higher gelatin content contributed to the stronger interaction of composite polymer film and was related with the acid value and the lower change in FTIR spectra under longer period of storage.

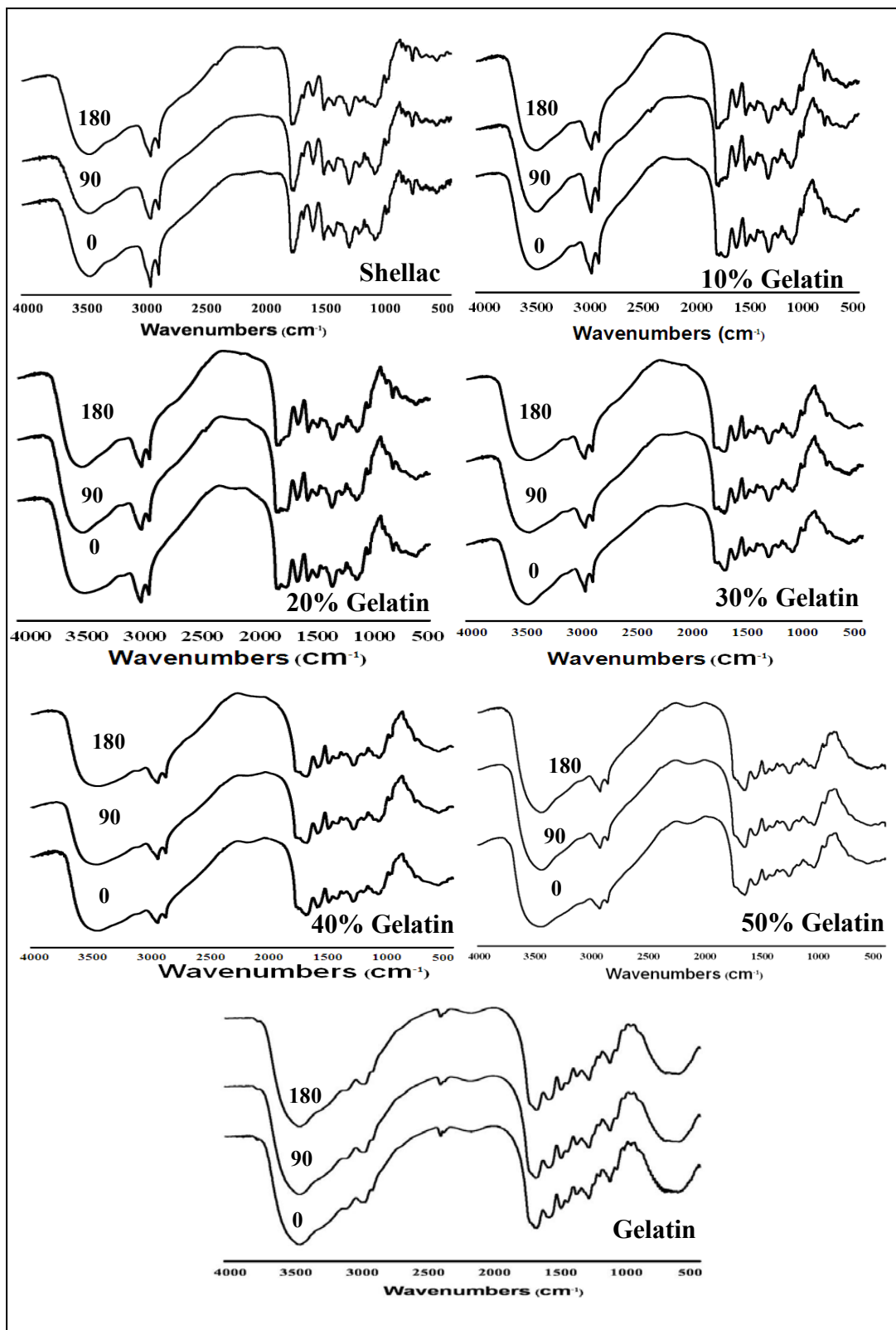


Figure 26 FTIR spectra of composite polymer films varying with the concentrations of gelatins upon storage at 40 °C, 75% RH for 180 days

## 2.4 Structure diagram

From the FTIR spectra, the change in acid value and the change in percentage of insoluble solid (IS) could be demonstrated the structure diagram of shellac in ammonium salt form and the composite polymer varying with the concentrations of gelatin upon storage for 180 days as shown in Figure 29-31. The polymerization of shellac in ammonium salt form was the result of the loss of ammonium ion, leading to the cross-linking formation of the esterification process as shown in structure diagram (Figure 27) and was related with the decrease in acid value, the increase in percent insoluble solid and the change in chemical structure of shellac upon storage for 180 days. In this study, the polymerization of ammoniated shellac could be protected by the electrostatic interaction between negative charge ( $\text{COO}^-$ ) from shellac and positive charge ( $\text{NH}_3^+$ ) from gelatin which could be explained by the structure diagram in Figure 28-29. The high concentrations of gelatin (30%, 40% and 50%) could prevent between the polymer chains of shellac from the cross-linking formation by the esterification process (Figure 29). The result was due to the higher gelatin content led to the higher polar groups giving the higher  $\text{NH}_2$  groups. It contributed to the high electrostatic interaction between  $\text{COO}^-$  from shellac and  $\text{NH}_3^+$  from gelatin. It was attributed to the high protection of the polymerization process into a higher extent compared to the single shellac or the shellac incorporation with the low concentration of gelatin. The incorporation of the low concentration of gelatin within the shellac network could not protect the polymerization at the active sites of shellac due to the reduction in electrostatic interaction of composite polymer after storage and the low amino groups of gelatin molecule, resulting in the polymerization of shellac by esterification process as displayed in structure model (Figure 28). The change in electrostatic interaction of composite polymer was correlated with the change in chemical structure and was reported by the reduction of the acid value and the extreme increase in the percent insoluble solid under longer period of storage.

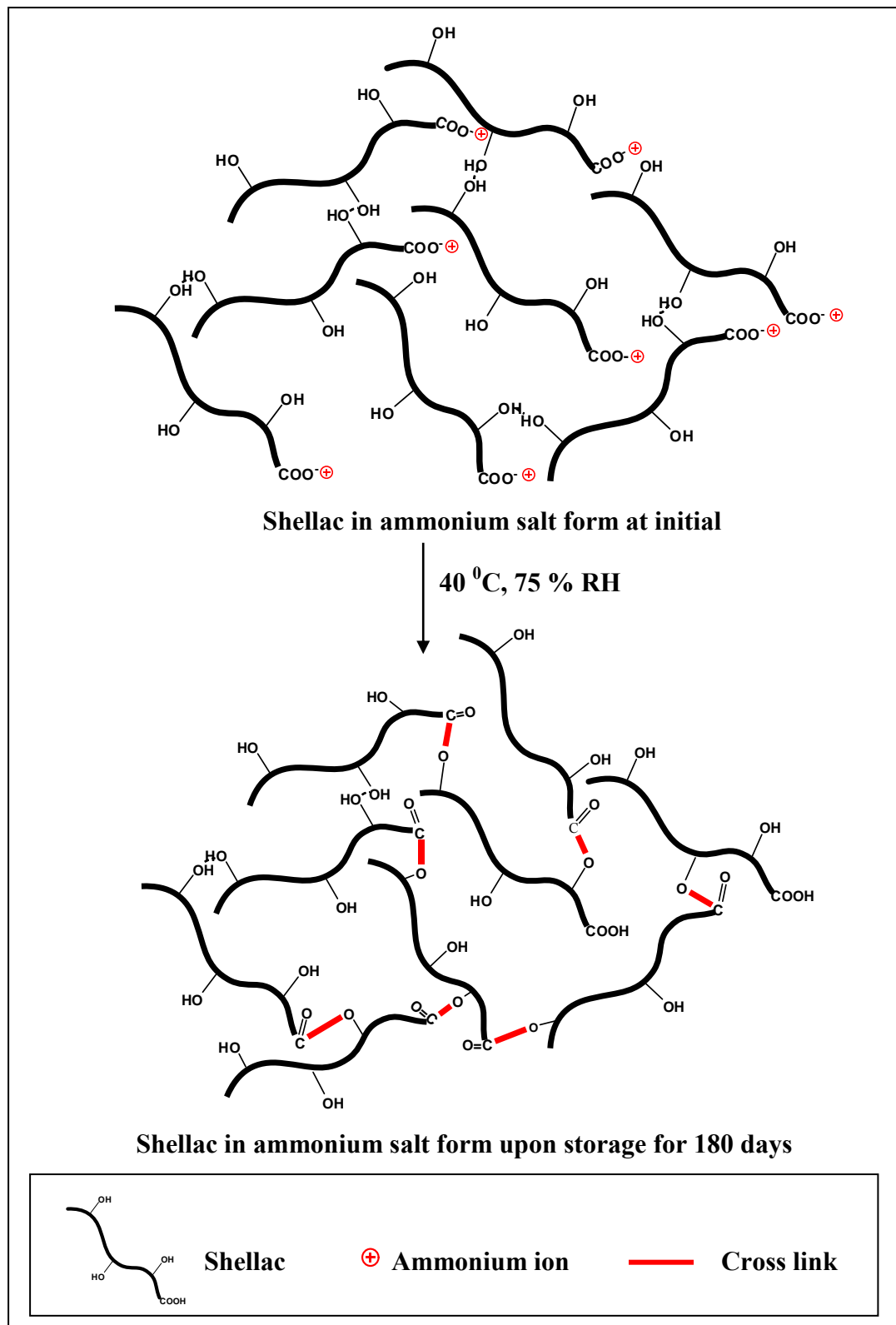


Figure 27 Structure diagrams of shellac in ammonium salt form upon storage at  $40^{\circ}\text{C}$  and 75% RH for 180 days

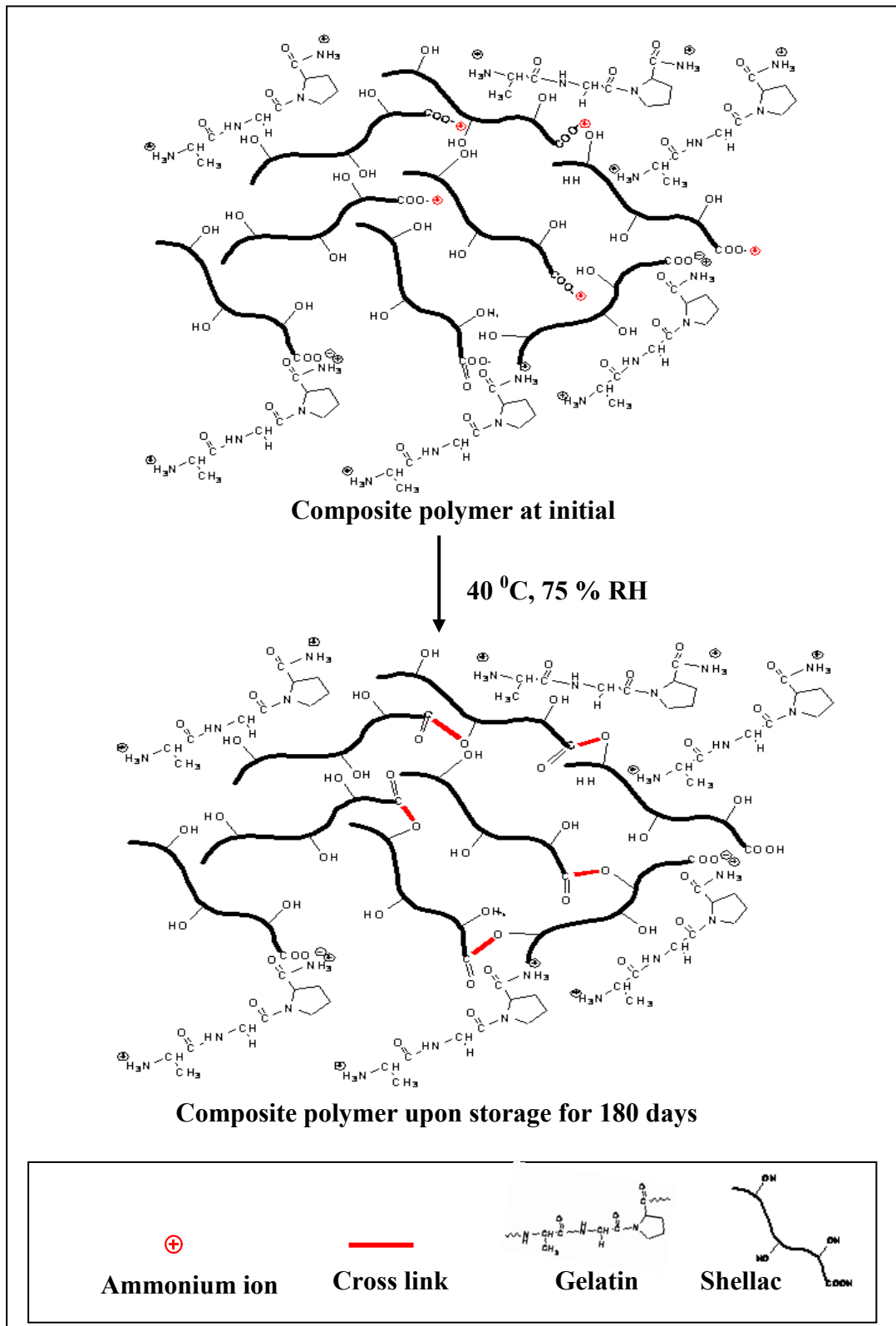


Figure 28 Structure diagrams of composite polymer with low concentration of gelatin upon storage at  $40\text{ }^{\circ}\text{C}$  and  $75\% \text{ RH}$  for 180 days

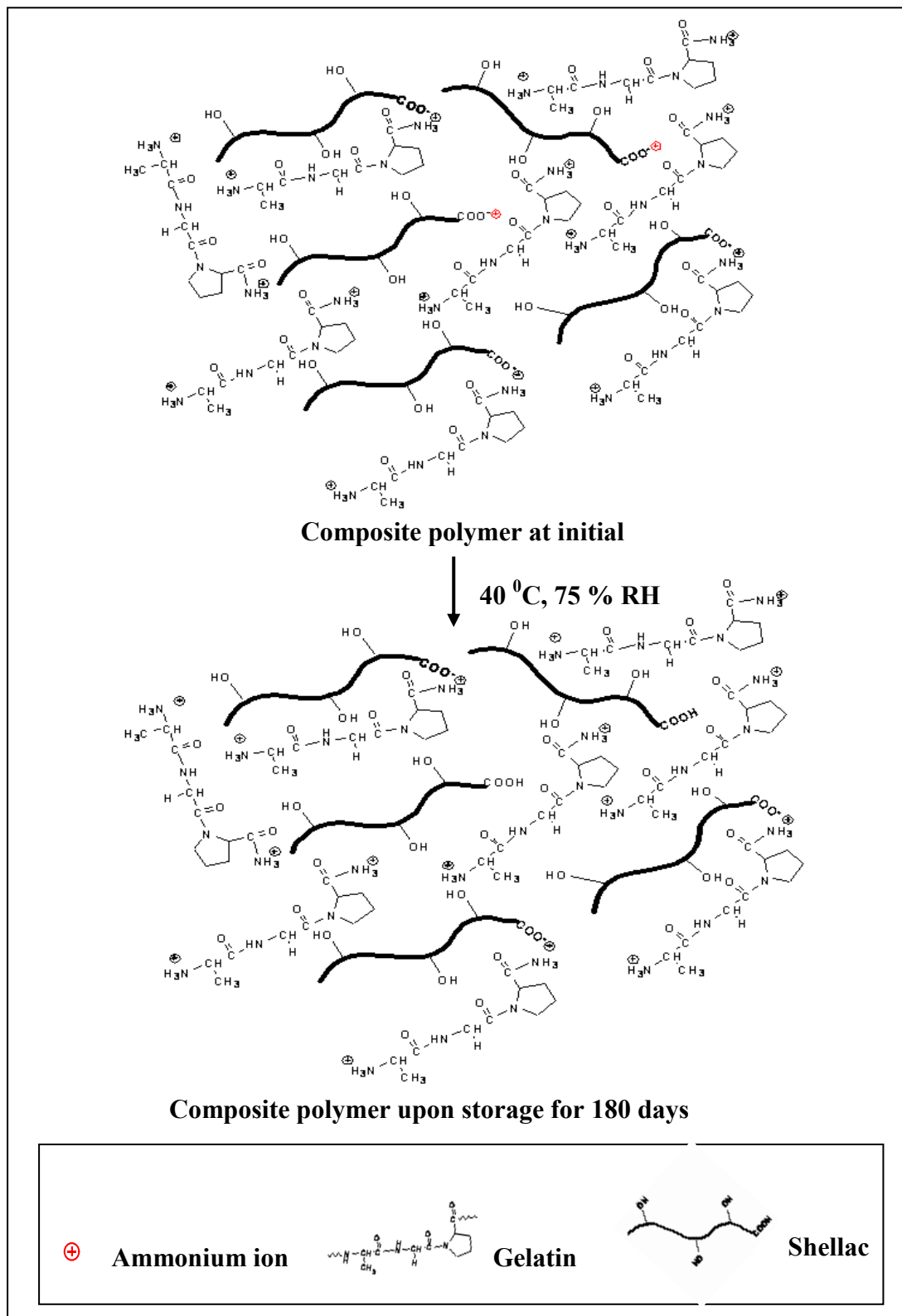


Figure 29 Structure diagrams of composite polymer with high concentration of gelatin upon storage at 40 °C and 75% RH for 180 days

## 2.5 Thermal analysis

The effect of storage time on the thermal behavior of composite polymer films was shown in Table 16. Upon storage for 180 days, the result was reported that the broad endothermic region curves tended to slight decrease in the lower temperature, resulting from the decrease in free water of composite polymer films and agreed with the reduction of the enthalpy as compared to the initial study. (The characteristic peak of all films were shown in appendix, Figure 53-54) The addition of gelatin could prevent the loss of free water more than the single shellac upon storage for 180 days which was confirmed by the higher enthalpy and the higher water loss of polymer films. The enthalpy and the water loss of shellac (0% gelatin) decreased from 67.65 to 50.05 J/g and decreased from 0.62 to 0.46%, respectively whereas the incorporation of gelatin at 50% gelatin decreased from 118.12 to 83.90 J/g and decreased from 4.25 to 3.72 % after storage for 180 days, respectively.

Table 16 Effect of gelatin content on thermal behavior of shellac and gelatin composite polymer films upon storage at 40 °C, 75% RH for 180 days

Content of gelatin (% w/w)	Enthalpy (J/g)			Water loss (%)		
	day 0	day 90	day 180	day0	day 90	day 180
0	67.50	64.16	50.05	0.62	0.74	0.46
10	77.65	62.44	53.99	1.08	1.14	0.51
20	91.20	79.17	64.58	2.50	1.70	0.78
30	104.73	73.26	77.98	2.69	1.58	2.01
40	115.80	76.44	79.44	4.12	2.76	3.44
50	118.12	79.76	83.90	4.25	3.01	3.72

## 2.6 Moisture content and water vapor permeability coefficient

Figure 30 shows the effect of storage time on the moisture content of single shellac film and composite polymer films with different concentrations of gelatin. Initially, the higher gelatin content led to the higher percent moisture content and increased from 8.61 to 12.74 % when gelatin was added up to 50%, resulting in the increase in the free water of film. Upon storage for 180 days, the moisture content of all films tended to decrease ( $P < 0.01$ ) from 8.61%, 9.56%, 10.10%, 10.62%, 12.46% and 12.74% to 5.03%, 5.12%, 5.95%, 5.57%, 6.23% and 6.66 % at the concentrations of 0, 10, 20, 30, 40 and 50%, respectively which was caused by the loss of free water of film as might be mainly attributed to the volatilization. The result was in agreement with the decrease in the surface free energy and the loss of free volume when measured using differential thermal analysis, attributing to the changed of all physicochemical properties of films.

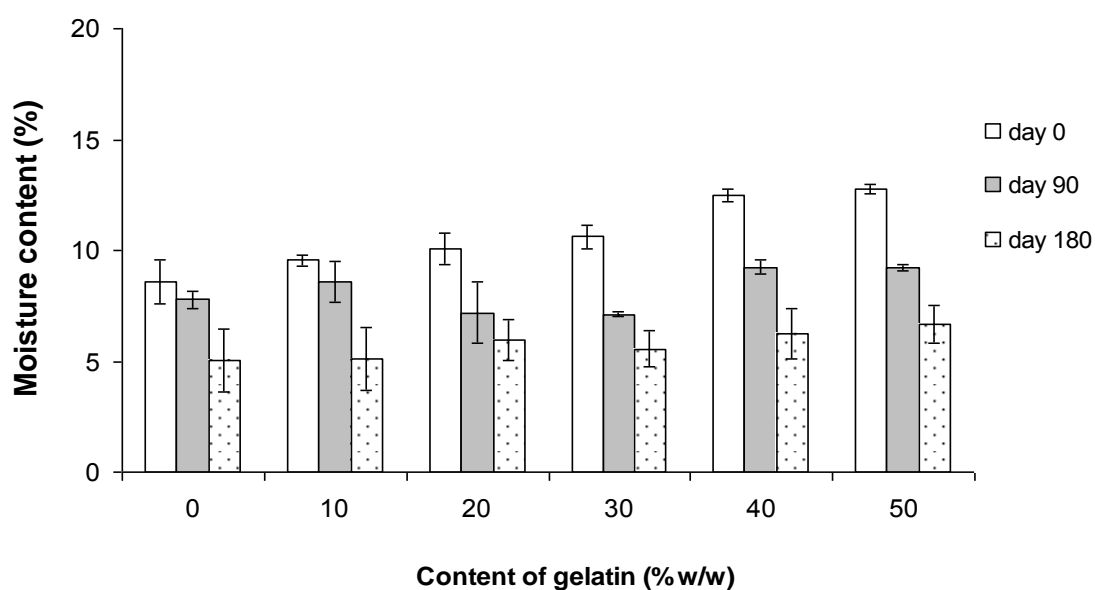


Figure 30 Effect of gelatin content on moisture content of shellac and gelatin composite polymer films upon storage at 40 °C, 75% RH for 180 days

Figure 31 shows the effect of storage time on WVPC after storage for 180 days. The WVPC tended to decrease significantly ( $p < 0.01$ ) for all composite polymer films and related to the decrease in water content. The WVPC decreased

from  $4.15 \times 10^{-8}$ ,  $4.43 \times 10^{-8}$ ,  $4.92 \times 10^{-8}$ ,  $5.34 \times 10^{-8}$ ,  $6.12 \times 10^{-8}$  and  $9.46 \times 10^{-8} \text{ gh}^{-1} \text{ m}^{-1} \text{ Pa}^{-1}$  to  $1.29 \times 10^{-8}$ ,  $2.95 \times 10^{-8}$ ,  $2.66 \times 10^{-8}$ ,  $2.49 \times 10^{-8}$ ,  $2.00 \times 10^{-8}$  and  $4.74 \times 10^{-8} \text{ gh}^{-1} \text{ m}^{-1} \text{ Pa}^{-1}$  at the concentrations of 0, 10, 20, 30, 40 and 50%, respectively upon storage for 180 days. The decrease in WVPC was due to the loss of water content in the polymer films, resulting in the higher tightness of composite polymer molecules, enabling to the difficulty in the permeation of moisture. The decrease in WVPC of shellac film was in agreement with the study of Manee Luangtana-anan et al. which reported that the reduction in WVPC of shellac caused the tighter structure of polymer, attributing to the lower of WVPC (Manee Luangtana-anan et al. 2007 : 687-692).

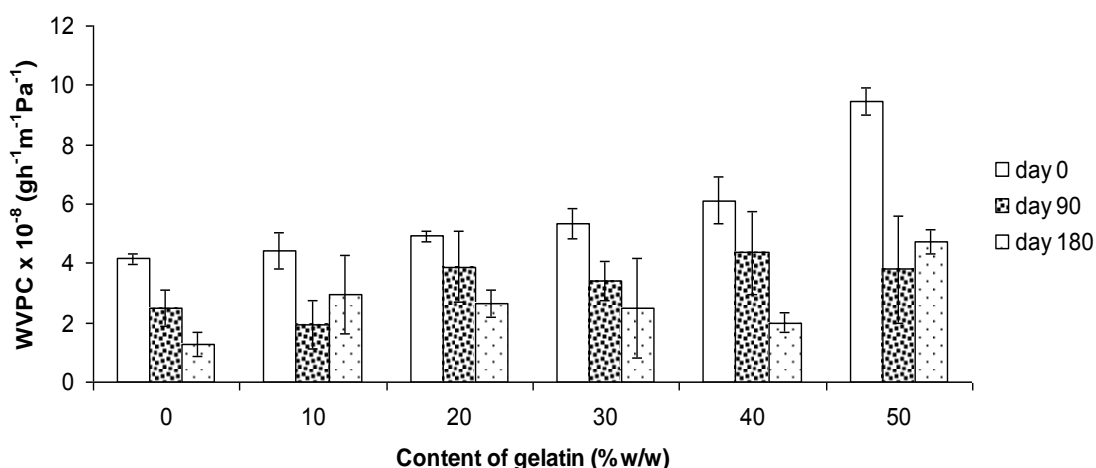


Figure 31 Effect of gelatin content on water vapor permeability coefficient of shellac and gelatin composite polymer films upon storage at 40 °C, 75% RH for 180 days

## 2.7 Mechanical properties

Figure 32 shows the effect of storage time on the puncture strength of composite polymer films after storage for 180 days. Upon storage for 180 days, all composite polymer films with different concentrations of gelatin extremely decreased the puncture strength from 3.61, 5.01, 8.51, 11.83, 14.07 and 15.58 MPa to 0.29, 0.21, 0.35, 0.81, 0.44 and 0.54 MPa at the concentrations of 0, 10, 20, 30, 40 and 50%,

respectively. The statistically extreme significant ( $P < 0.01$ ) change in the puncture strength of single shellac film was the result of the loss of free water in the films while of shellac with the incorporation of different concentrations of gelatin, resulting from the reduction in free volume of polymer and the electrostatic interaction between shellac and gelatin, correlated with the loss of percent moisture content in composite polymer film, the decrease in the surface free energy, percent polarity and the change in chemical structure of film upon 180 days of storage. The lower mechanical strength of shellac under longer period of storage was in agreement with other report (Manee Luangtana-anan et al. 2007 : 687-692).

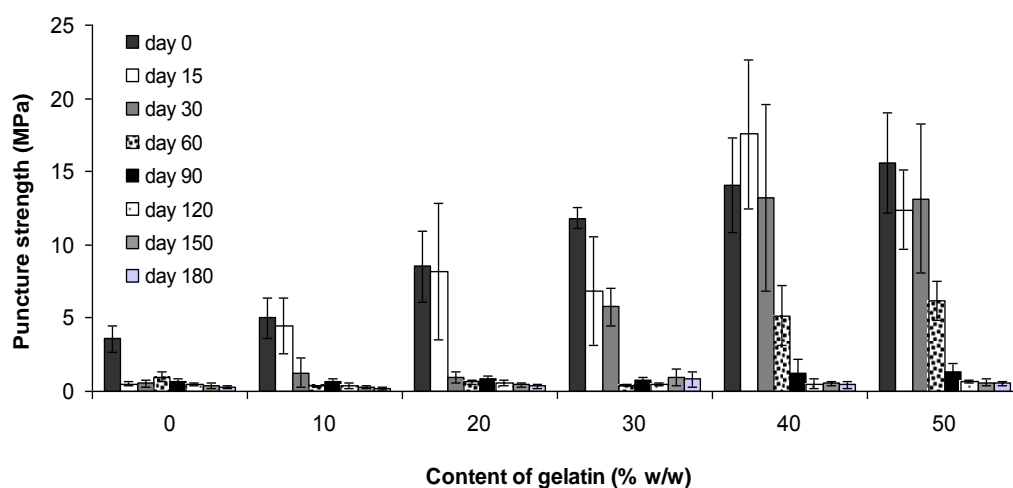


Figure 32 Effect of gelatin content on mechanical properties (puncture strength) of shellac and gelatin composite polymer films upon storage at 40 °C, 75% RH for 180 days

The effects of storage on the percentage of elongation of composite polymer films varied with the concentrations of gelatin were shown in Figure 33. The composite polymer could prevent the decrease in percentage of elongation during storage up to 60 days and further storage giving the lower percentage of elongation. Upon storage for 180 days, all composite polymer films with different proportions of gelatin extremely decreased the percent elongation from 3.80, 6.51, 12.89, 19.65, 26.66 and 32.47 % to 1.08, 1.09, 0.67, 0.84, 0.52 and 0.84 % at the concentrations of 0, 10, 20, 30, 40 and 50%, respectively. The lower percent elongations of all polymer

films were a result of the loss of free water which was indicated by the reduction of the water content and agreed with the change in the other parameters. The lower elongation under longer period of storage was in accordance with other studies (Heng et al. 2003 : 334-344; Manee Luangtana-anan et al. 2007 : 687-692). Therefore, the result could be concluded that the composite polymer films based on shellac and gelatin could not prevent the reduction in the mechanical properties of shellac for 180 days of storage due to the loss of free water and the reduction of electrostatic interaction at the longer periods of time.

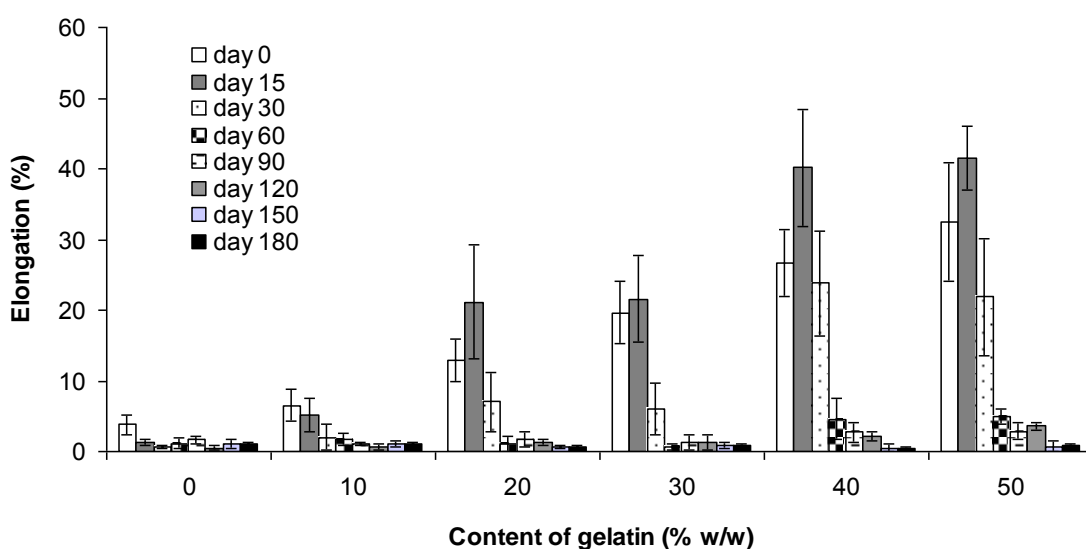


Figure 33 Effect of gelatin content on mechanical properties (percentage of elongation) of shellac and gelatin composite polymer films upon storage at 40 °C, 75% RH for 180 days

## 2.8 Powder X-ray diffraction (PXRD)

Figure 34 shows the effect of storage times on the change in PXRD pattern of composite polymers varied with the concentrations of gelatin. The result demonstrated that the PXRD pattern of all composite polymer films did not change upon storage for 180 days.

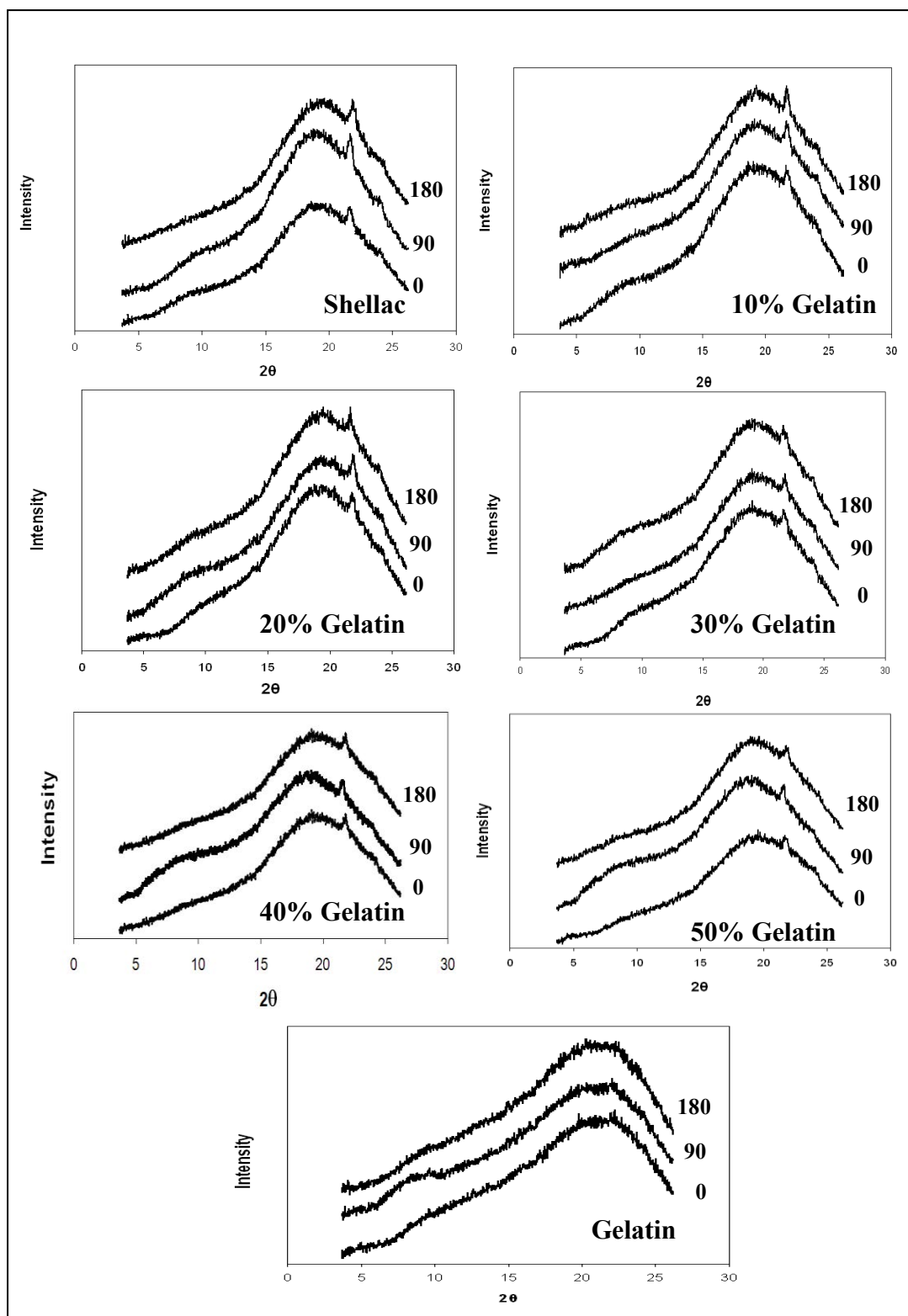


Figure 34 PXR D patterns of composite polymer films varying with the concentrations of gelatin upon storage at 40 °C, 75% RH for 180 days

## 2.9 Summary

In conclusion, the decline in use of shellac as food and pharmaceutical film coating was due to the polymerization at hydroxyl and carboxyl groups of shellac, resulting in the instability. The formation of composite polymer with gelatin at the high concentrations (30%, 40% and 50%) could protect at the active sites of shellac from the cross linking formation of the esterification process by electrostatic interaction between negative charge ( $\text{COO}^-$ ) from shellac and positive charge ( $\text{NH}_3^+$ ) from gelatin upon 180 days of storage. Therefore, the attempt to improve the stability in term of polymerization process of shellac by the formation of composite polymer between shellac and gelatin could be achieved. However, the mechanical properties could not withstand the storage time, resulting from the loss of free water and the reduction in the electrostatic interaction between shellac and gelatin. Hence, further investigation was required to improve the stability in term of mechanical properties of composite polymer film under longer storage by adding plasticizer as described in topic 3.

## 3. Effect of types and concentrations of plasticizers on mechanical properties and stability of composite polymer based on shellac and gelatin

In previous study, the shellac could be prepared by the formation of composite polymer with the appropriate concentrations of gelatin at 30%, 40% and 50% as these concentrations could protect the polymerization of shellac upon 180 days of storage and prevented the reduction of mechanical properties of shellac upon storage. However, the mechanical properties of composite polymers could stabilize only 60 days of storage and further storage attributed to the high brittleness and low flexibility, indicated by the extreme decrease in the puncture strength and the % elongation. Therefore, the purpose of this study was to enhance the mechanical properties of composite polymer based on shellac and gelatin by adding with the suitable plasticizer. In this study, 40% gelatin was appropriate concentration for further study to the effect of types and concentrations of plasticizers on the mechanical properties and stability composite polymer film since at 30 % gelatin showed a lower stabilized effect and at 50% gelatin showed the higher WVPC giving

the lower protection. Two types of plasticizers i.e., polyethylene glycol (PEG) and diethyl phthalate (DEP) represented hydrophilic and hydrophobic plasticizers at the concentration of 5 and 10%, respectively. The single shellac and the composite polymer with and without plasticizers were then compared to investigate for physicochemical properties as shown in Table 17-21 and Figure 35-43.

### **3.1 Wettability and surface free energy**

The effect of types and concentrations of plasticizers on the wettability of composite polymer upon storage for 180 days were shown in Table 17. The result demonstrated that the higher wettability indicated by the lower contact angle of composite polymer was obtained as the addition of polyethylene glycol due to the influence of hydrophilic plasticizer and the higher affinity of hydrophilic plasticizer whereas the opposite effect was obtained when diethyl phthalate was added. In addition, the higher concentrations of polyethylene glycol gave the lower contact angle when the water was used as wetting liquid, attributing to the higher wettability of composite polymer film whereas the higher contact angle was reported for the higher diethyl phthalate concentrations, resulting in the lower hydrophilicity of film. Upon storage for 180 days, unplasticized and plasticized film tended to decrease in the wettability of all films, indicated by the increase in the contact angle of film when the water was used as wetting liquid. The contact angle of shellac film, unplasticized composite polymer film and plasticized composite polymer films with PEG 400 5%, PEG 400 10%, DEP 5% and DEP 10% increased from 81.39, 70.89, 67.55, 65.74, 76.12, 79.64 degree to 92.01, 76.50, 71.87, 69.35, 85.06, 88.17 degree, respectively. The result exhibited the decrease in the hydrophilicity of composite polymer films on longer period of storage.

The change in the contact angle of all films had an influence on the change in the surface free energy and percent polarity of all unplasticized and plasticized film as shown in Table 18-21. The higher surface free energy and the higher % polarity of composite polymer films increased as the increase in PEG 400 concentrations due to the higher OH group, contributing to the stronger hydrogen bonding at the polymer chain whereas the lower surface free energy and lower polarity were obtained as the addition of the higher diethyl phthalate (DEP)

concentrations. The result was in accordance with the other study (Oh and Luner 1999 : 203-219). Upon storage for 180 days, the surface free energy of all plasticized composite polymer films tended to slightly decrease. The surface free energy of films decreased from 37.28, 41.46, 43.81, 46.16, 39.33 and 37.96 mN/m to 34.32, 38.84, 41.62, 43.51, 35.91 and 34.94 mN/m for the single shellac, unplasticized composite polymer and plasticized composite polymer with PEG 400 5%, PEG 400 10%, DEP 5% and DEP 10%, respectively upon storage for 180 days. The reduction in surface free energy upon storage was in accordance with the decrease in wettability. In addition, the reduction in hydrophilicity could be demonstrated by the reduction in percent polarity as shown in Figure 50. The percent polarity tended to slightly decrease for plasticized composite polymer films with PEG 400 of both concentrations while shellac film, unplasticized composite film and plasticized composite polymer film with DEP of both concentrations extremely decreased. The decrease in percent polarity of plasticized film with PEG 5%, PEG 10% , DEP 5% and DEP 10% was from 41.46%, 44.47%, 38.92% and 30.00 % to 33.47 %, 39.65%, 21.27% and 20.08%, respectively while shellac film and unplasticized composite polymer film was from 26.23%, 39.85%, to 14.98 %, 28.17 %, after storage for 180 days.

Table 17 Effect of types and concentrations of plasticizers on wettability of composite polymer films (CF) based on shellac and gelatin upon storage at 40 °C, 75% RH for 180 days when water was used at standard liquid

Type of polymer film	Contact angle (degree)		
	day 0	day 90	day 180
SHL	81.39 ± 1.32	83.34 ± 3.30	92.01 ± 1.18
CF	70.89 ± 0.72	75.61 ± 0.89	76.50 ± 1.20
CF + PEG 400 5%	67.55 ± 0.77	69.71 ± 0.50	71.87 ± 1.35
CF + PEG 400 10%	65.74 ± 0.93	67.25 ± 1.22	69.35 ± 0.53
CF + DEP 5%	76.12 ± 1.90	81.12 ± 0.61	85.06 ± 4.66
CF + DEP 10%	79.64 ± 3.61	84.69 ± 1.62	88.17 ± 0.64

Table 18 Effect of types and concentrations of plasticizers on surface free energy of shellac and gelatin composite polymer films upon storage at 40 °C, 75% RH for 180 days

Type of polymer film	Total Surface free energy ( $\gamma^T_s$ , mN/m)		
	day 0	day 90	day 180
SHL	37.28 ± 1.96	34.96 ± 3.96	34.32 ± 4.05
CF	41.46 ± 1.28	39.61 ± 2.79	38.84 ± 3.37
CF + PEG 400 5%	43.81 ± 1.26	43.05 ± 1.76	41.62 ± 2.10
CF + PEG 400 10%	46.16 ± 1.25	44.68 ± 2.14	43.51 ± 2.62
CF + DEP 5%	39.33 ± 2.22	37.32 ± 2.03	35.91 ± 2.72
CF + DEP 10%	37.96 ± 1.09	35.94 ± 0.89	34.94 ± 1.36

Table 19 Effect of types and concentrations of plasticizers on dispersive force of shellac and gelatin composite polymer films upon storage at 40 °C, 75% RH for 180 days

Type of polymer film	Dispersive force ( $\gamma^D_s$ , mN/m)		
	day 0	day 90	day 180
SHL	27.50 ± 2.49	25.99 ± 5.72	29.18 ± 2.67
CF	24.94 ± 2.56	27.89 ± 3.73	27.90 ± 1.67
CF + PEG 400 5%	27.25 ± 1.50	28.22 ± 3.48	26.55 ± 2.28
CF + PEG 400 10%	26.27 ± 1.02	28.48 ± 1.94	24.72 ± 2.32
CF + DEP 5%	24.94 ± 2.28	27.65 ± 3.01	28.28 ± 3.20
CF + DEP 10%	24.76 ± 1.18	27.07 ± 1.28	27.94 ± 2.06

Table 20 Effect of types and concentrations of plasticizers on polar force of shellac and gelatin composite polymer films upon storage at 40 °C, 75% RH for 180 days

Type of polymer film	Polar force( $\gamma^P_s$ , mN/m)		
	day 0	day 90	day 180
SHL	9.78 ± 2.67	8.97 ± 2.05	5.14 ± 1.28
CF	16.52 ± 2.54	11.72 ± 1.56	10.94 ± 2.34
CF + PEG 400 5%	18.88 ± 1.83	17.53 ± 1.95	15.06 ± 3.23
CF + PEG 400 10%	21.22 ± 2.17	19.01 ± 2.03	18.78 ± 2.48
CF + DEP 5%	14.39 ± 1.78	9.67 ± 2.36	7.63 ± 1.05
CF + DEP 10%	13.20 ± 1.29	8.87 ± 0.83	7.00 ± 2.51

Table 21 Effect of types and concentrations of plasticizers on polarity of shellac and gelatin composite polymer films upon storage at 40 °C, 75% RH for 180 days

Type of polymer film	Polarity (%)		
	day 0	day 90	day 180
SHL	26.23 ± 5.33	25.66 ± 3.52	14.98 ± 5.86
CF	39.85 ± 0.42	29.59 ± 7.01	28.17 ± 5.09
CF + PEG 400 5%	41.46 ± 1.91	35.85 ± 1.90	33.47 ± 2.25
CF + PEG 400 10%	44.47 ± 6.08	41.62 ± 2.86	39.65 ± 4.88
CF + DEP 5%	38.92 ± 4.26	25.94 ± 6.59	21.27 ± 6.73
CF + DEP 10%	30.00 ± 5.20	24.70 ± 2.47	20.08 ± 3.89

### 3.2 Moisture content and water vapor permeability coefficient

Figure 35 shows the effect of storage times on the moisture content of single shellac film and composite polymer films with and without plasticizers. Initially, the addition of all types and concentrations of plasticizers affected the increase in the water content of films and the values were 8.61, 12.46, 14.27, 16.78, 12.68 and 14.96 % for the single shellac, unplastitized composite polymer film and plasticized composite polymer films with PEG 400 5%, PEG 400 10%, DEP 5% and DEP 10%, respectively, contributing to the higher free volume and plasticizing effect of films. Upon storage for 180 days, plasticized composite polymer films with PEG 400 of both concentrations showed the slight decrease in the % moisture content while the single shellac film and unplastitized and plasticized films with DEP of both concentrations extremely decreased ( $P < 0.01$ ), resulting in the reduction of puncture strength and the percentage of elongation of polymer film due to the loss of free water of film. It might be mainly attributed to the volatilization that was in agreement with the decrease in the surface free energy and percent polarity of film.

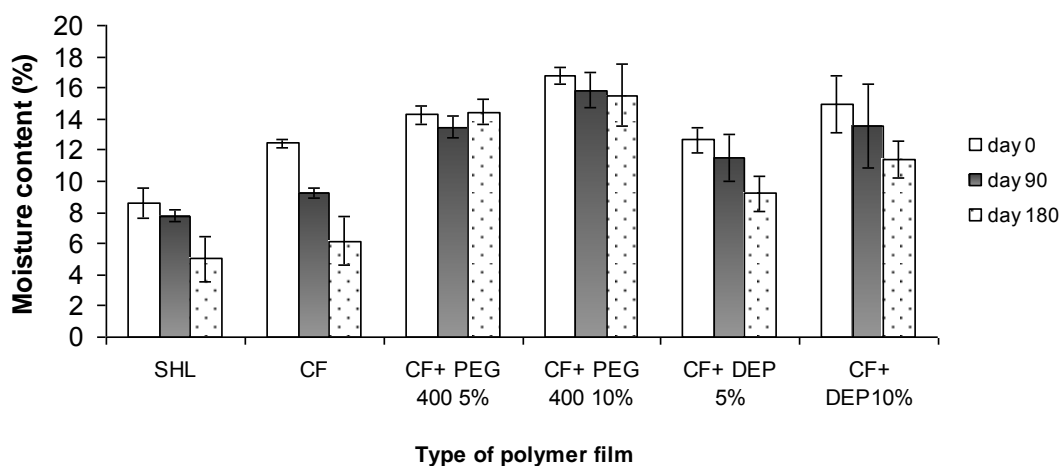


Figure 35 Effect of types and concentrations of plasticizers on moisture content of composite polymer films based on shellac and gelatin upon storage for 180 days at 40 °C, 75% RH

Figure 36 shows the effect of types and concentrations of plasticizers on water vapor permeability coefficient (WVPC) of composite polymer films upon storage for 180 days. Initially, the addition of PEG 5 and 10% tended to increase the WVPC whereas the addition of 5 and 10 % DEP lowered the WVPC. This was the result of the addition of hydrophilic nature of polyethylene glycol, and hydrophobic nature of diethyl phthalate. The hydrophilic plasticizer was able to capture higher water content while the opposite effect was shown for hydrophobic plasticizer. The result was in accordance with some other studies (Saettone et al. 1995 : 83-88; Yang and Paulson 2000 : 563-570). Yang & Paulson found that the addition of some plasticizers, e.g., glycerol, sorbitol, and polyethylene glycol, had increased the WVPC of films as prepared from the various polymers due to the high aqueous solubility of plasticizer (Yang and Paulson 2000 : 563-570). Saettone et al. indicated that the use of polyethylene glycol could increase the water vapor permeability of hydroxypropyl methylcellulose (HPMC) film whereas castor oil and dibutyl phthalate reduced the water vapor permeability (Saettone et al. 1995 : 83-88). As the higher concentrations of PEG, the higher WVPC was obtained due to the higher hydrophilicity, indicated by the higher surface free energy and percent polarity of composite polymer film. In the opposite result, the lower WVPC was observed when the higher concentrations of DEP. The effect of concentrations of plasticizers was in accordance with some other worked (Cuq et al. 1997 : 622-626; Mali et al. 2006 : 453-460). Mali et al. found that the increase in hydrophilicity of the starch films at the higher glycerol concentrations, resulting from the more active sites of hydrophilic hydroxyl groups for exposing to the water molecules (Mali et al. 2006: 453-460). Cuq et al. reported that the increase in the concentration of hydrophilic plasticizer, attributing to the increase in the WVPC of hygroscopic polymer films, due to the reorganization of the polymer network, with consequent increase in the free volume (Cuq et al. 1997 : 622-626).

Upon storage for 180 days, the WVPC decreased slightly for all plasticized films whereas the unplasticized films showed the higher reduction. The reduction of WVPC might be a result of the loss of free volume causing the tighter structure of film, attributing to the lower of WVPC and was in accordance with the loss of moisture content. The result was in agreement with other report (Manee

Luangtana-anan et al. 2007 : 687-692; Manee Luangtana-anan et al. 2010 : 12934-12940) which found that the higher storage, the reduction in WVPC of plasticized shellac film was obtained, resulting from the tighter structure of polymer, attributing to the lower of WVPC.

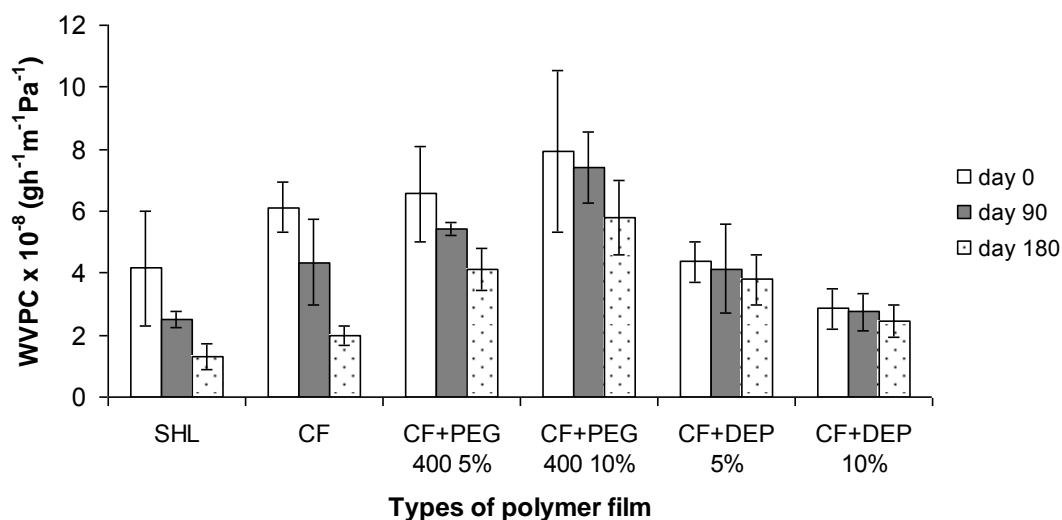


Figure 36 Effect of types and concentrations of plasticizers on WVPC of composite polymer films based on shellac and gelatin upon storage for 180 days at 40 °C, 75% RH

### 3.3 Mechanical properties

Figure 37 shows the effect of types and concentrations of plasticizers on the mechanical properties of composite polymer films upon storage for 180 days. Initially, the addition of both types and concentrations of plasticizers affected the decrease in the puncture strength and increase in percent elongation of composite polymer films. The puncture strength values were 3.61, 14.07, 11.40, 3.71, 12.28, 7.34 MPa while the percentage of elongation values were 3.80, 26.26, 63.53, 134.28, 50.69, 98.17 % for the single shellac, unplasticized composite polymer and plasticized composite polymer with PEG 400 5%, PEG 400 10%, DEP 5% and DEP 10%, respectively. The mechanical properties of all plasticized films were changed significantly ( $P < 0.01$ ) when compared to the single shellac film and unplasticized composite polymer film, suggesting that the types of plasticizers had an influence on

the mechanical properties of films. PEG 400 showed the higher plasticizing effect than DEP due to PEG 400 had more polar group (indicated by percent polarity) and high soluble in the water than DEP which could insert into the composite polymer network attributing to the decrease in the intermolecular attraction of composite polymer chains. The result was in agreement with other reports (McHugh et al. 1994 : 416-419; Yang and Paulson 2000 : 563-570; Manee Luangtana-anan et al. 2007 : 687-692). Therefore, the plasticizing effect was dependent on the polar groups, size and total number of polar group of plasticizers. Apart from both types of plasticizers, the concentrations of both plasticizers were also investigated to affect on the mechanical properties of composite polymer films. The higher concentrations of all plasticizers, the lower puncture strength and the higher percentage of elongation were obtained, attributing to the extreme increase in the flexibility and the decrease in strength of composite polymer film. The result was due to the plasticizers reduced the intermolecular attraction between the shellac and gelatin and within the polymer chains and was in accordance with other studies (Yang and Paulson 2000: 563-570; Qussi and Suess 2006 : 403-412).

Upon storage, all plasticized composite polymers tended to increase the puncture strength due to some functional group of plasticizer chain could be attributed to a development of hydrogen bonds between composite polymer and plasticizer, replacing the polymer to polymer interactions (Manee Luangtana-anan et al. 2010 : 12934-12940). Polyethylene glycol could attract the hydrogen bonding between polymer chains in a higher extent than diethyl phthalate, due to the higher polar group leading to the increase in puncture strength upon storage while DEP at 5 and 10% could increase the puncture strength upon storage for 60 days and further storage gave the decrease in the puncture strength due to the lower polar group of DEP. It resulted in the lower hydrogen bond attraction between polymer and plasticizers. In addition all plasticized films showed the higher elongation and the influence of storage time had a lower effect on the reduction in percentage of elongation than unplasticized films. After storage for 180 days all plasticized composite films still had sufficient mechanical properties. The result could be concluded that the plasticizers could

improve the poor mechanical properties of composite polymer films upon storage for 180 days.

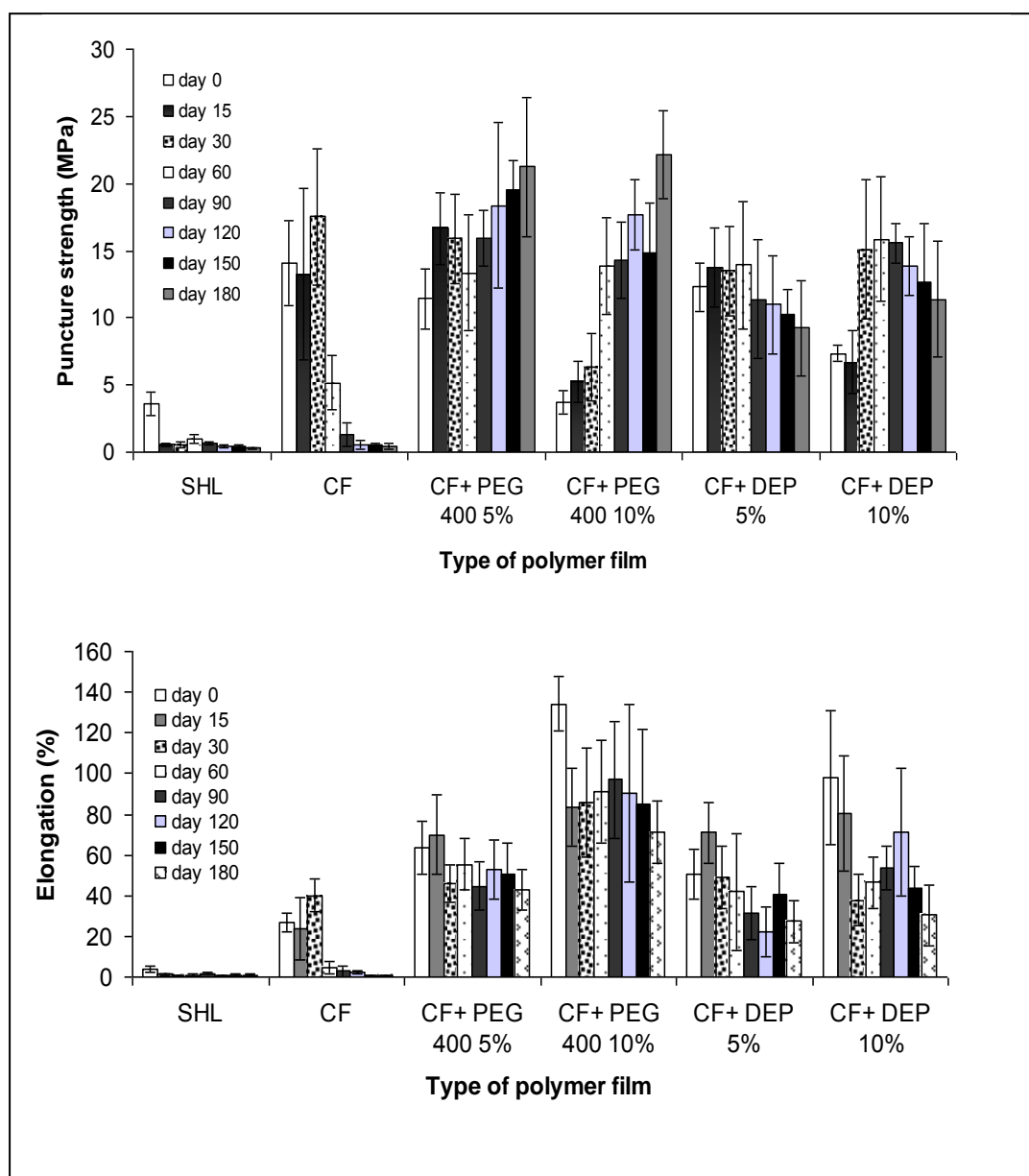


Figure 37 Effect of types and concentrations of plasticizers on mechanical properties of composite polymer films based on shellac and gelatin upon storage for 180 days at 40 °C, 75% RH

### 3.4 Powder X-ray diffraction

Figure 38 shows the PXRD patterns of shellac and unplasticized and plasticized composite polymer films with PEG 400 5%, PEG 400 10%, DEP 5% and DEP 10%, respectively. The result demonstrated that the addition of plasticizers of both types and concentrations in the composite polymer film did not change the PXRD patterns. However, the lower puncture strength was the result of the reduction in the intermolecular attraction of composite polymer films which was confirmed by other physicochemical properties and agreed with the other reports (Yang and Paulson 2000: 563-570; Manee Luangtana-et al. 2007 : 687-692; Cao et al. 2009 : 729-735).

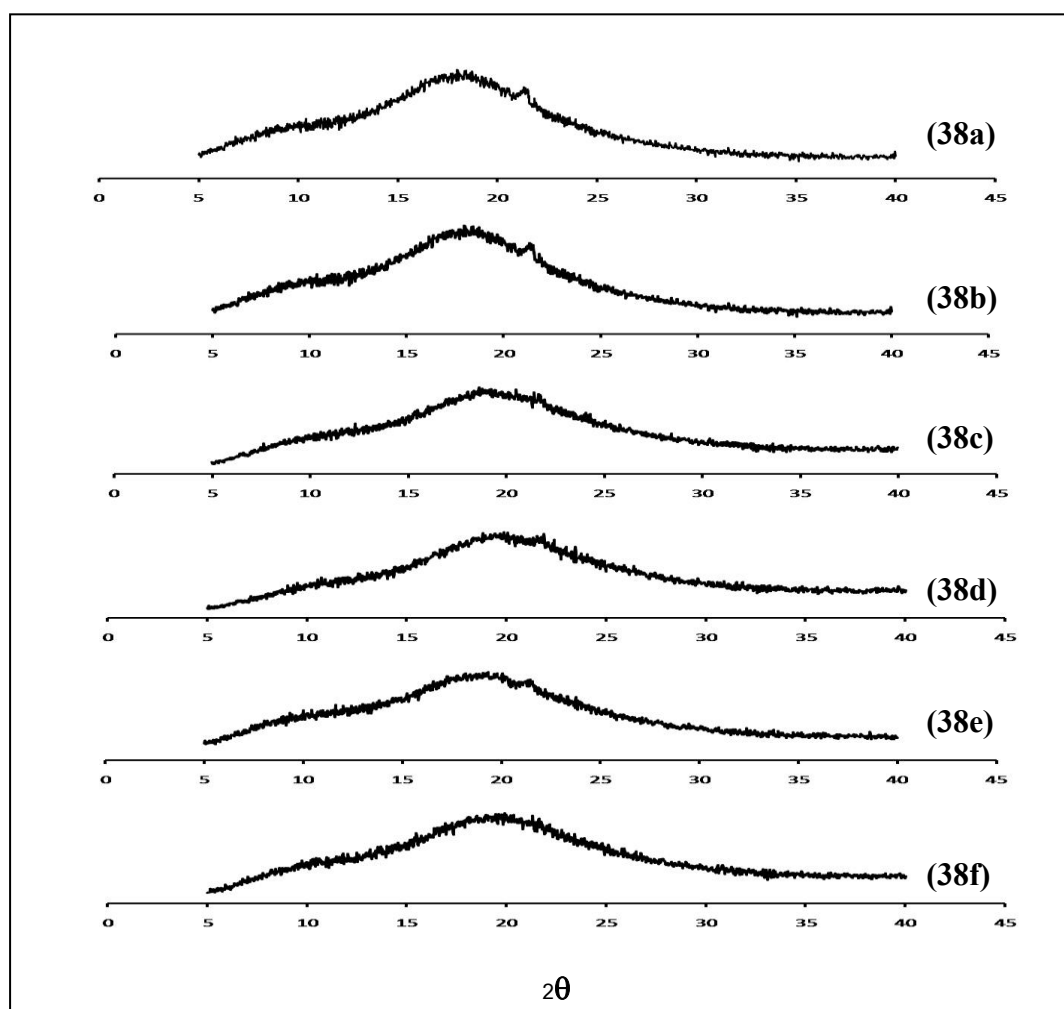


Figure 38 PXRD patterns of single shellac film (38a), unplasticized composite polymer film (38b), plasticized composite polymer films with PEG 400 5% (38c), PEG 400 10% (38d), DEP 5% (38e) and DEP 10% (38f)

### 3.5 Fourier transformed infrared (FTIR) spectroscopy

Figure 39 shows the FTIR spectrum of shellac, gelatin, unplasticized composite polymer and plasticized composite polymer with polyethylene glycol and polyethylene glycol spectrum while the spectrum of plasticized composite polymer with DEP was displayed in Figure 40. Polyethylene glycol (39f) showed the absorption band at 3300-3400  $\text{cm}^{-1}$  (O-H stretching), 2884  $\text{cm}^{-1}$  (C-H stretching), 1645  $\text{cm}^{-1}$  ( $\text{CH}_2$  bending) and 1474  $\text{cm}^{-1}$  ( $\text{CH}_3$  bending) and 1053  $\text{cm}^{-1}$  (C-O stretching) while the FTIR spectrum of diethyl phthalate was found the characteristic peak at 2981  $\text{cm}^{-1}$  (C-H stretching), 1727  $\text{cm}^{-1}$  (C=O stretching), 1606  $\text{cm}^{-1}$  (C=C conjugation), 1130  $\text{cm}^{-1}$  and 1074  $\text{cm}^{-1}$  (C-O stretching) as displayed in Figure 40f. The addition of plasticizers in the composite polymer films differently affected the change in the attraction of composite polymer films. The addition of polyethylene glycol was attributed to the decrease in the broad band spectrum at 3200-3500  $\text{cm}^{-1}$  of composite polymer film due to the OH stretching of shellac and N-H stretching of gelatin and the change at 1645  $\text{cm}^{-1}$  due to the  $\text{CH}_2$  bending of polyethylene glycol and Amide I of gelatin while the addition of diethyl phthalate decreased the broad band spectrum at 3200-3500  $\text{cm}^{-1}$  of composite polymer and the change at 1727  $\text{cm}^{-1}$  due to the carbonyl stretching (C=O) of diethyl phthalate and 1130  $\text{cm}^{-1}$  and 1074  $\text{cm}^{-1}$  due to the C-O stretching of diethyl phthalate. Therefore, from FTIR spectra of plasticized composite polymer films could prove that all plasticizers were inserted within the composite polymer network. The decrease in broad band spectrum of all plasticized composite polymer film at 3200-3500  $\text{cm}^{-1}$  may be a result of the reduction in the intermolecular attraction of composite polymer films, attributing to the lower strength and the higher flexibility of composite polymer films.

Upon storage for 180 days, the FTIR spectra of plasticized composite films with PEG 400 of both concentrations did not change, exhibiting the higher stability of film and the lower loss of plasticizer due to the high molecular weight of PEG (Figure 41) while the plasticized composite film with DEP of both concentrations showed the disappeared of peak at 1727  $\text{cm}^{-1}$  due to C=O stretching, 1130  $\text{cm}^{-1}$  and 1074  $\text{cm}^{-1}$  due C-O stretching. The disappeared of peak was due to the loss of plasticizer and high volatilization. The loss of plasticizers and higher

volatilization of DEP resulted from the lower molecular weight attributing to the poor protection of DEP at the active sites of composite polymer film and hence a high polymerization among these groups.

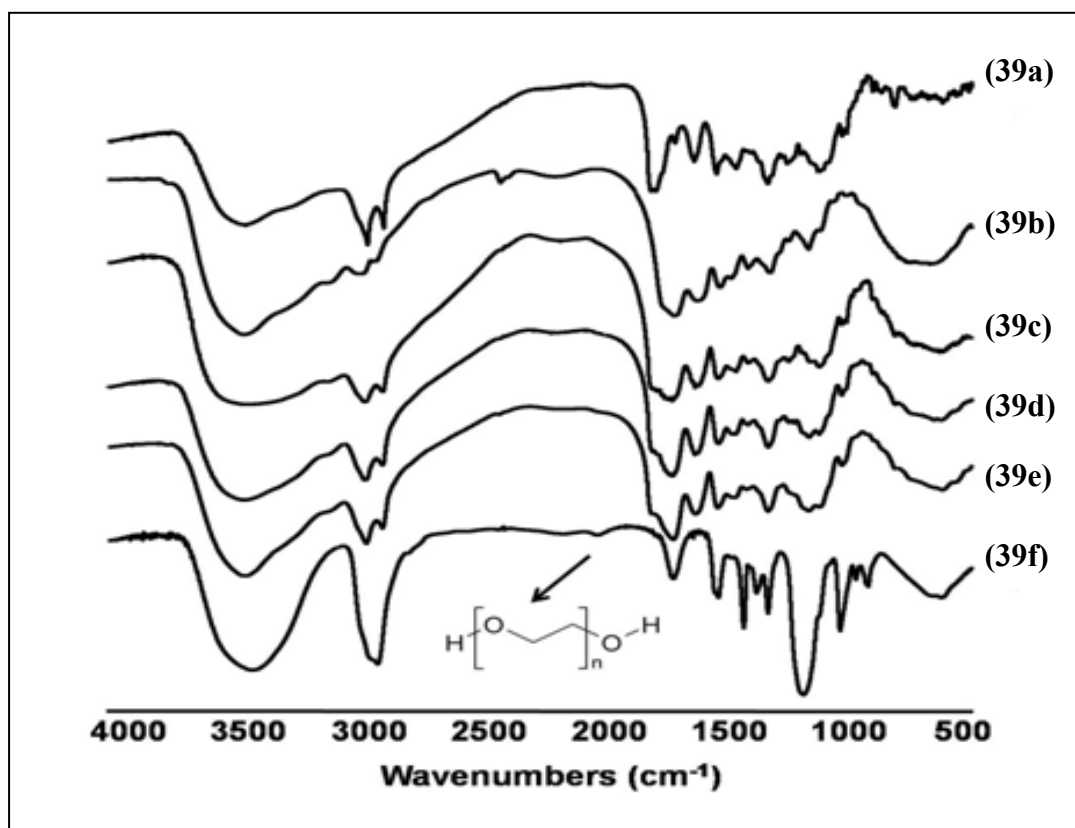


Figure 39 FTIR spectra of single shellac film (39a), single gelatin film (39b), composite polymer film without plasticizer (39c) and composite polymer films with PEG 400 5% (39d), PEG 400 10% (39e) and polyethylene glycol 400 (PEG, 39f)

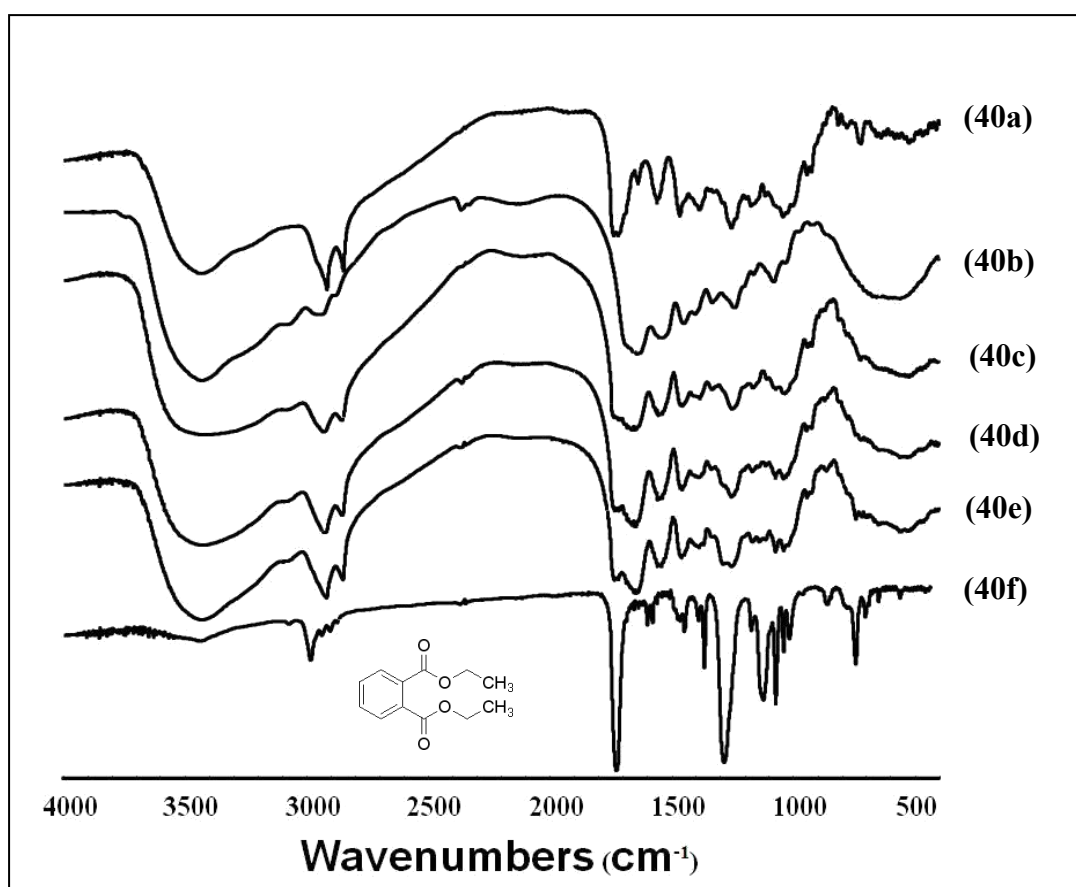


Figure 40 FTIR spectra of single shellac film (40a), single gelatin film (40b), composite polymer film without plasticizer (40c) and composite polymer films with DEP 5% (40d), DEP 400 10% (40e) and diethyl phthalate (DEP, 40f)

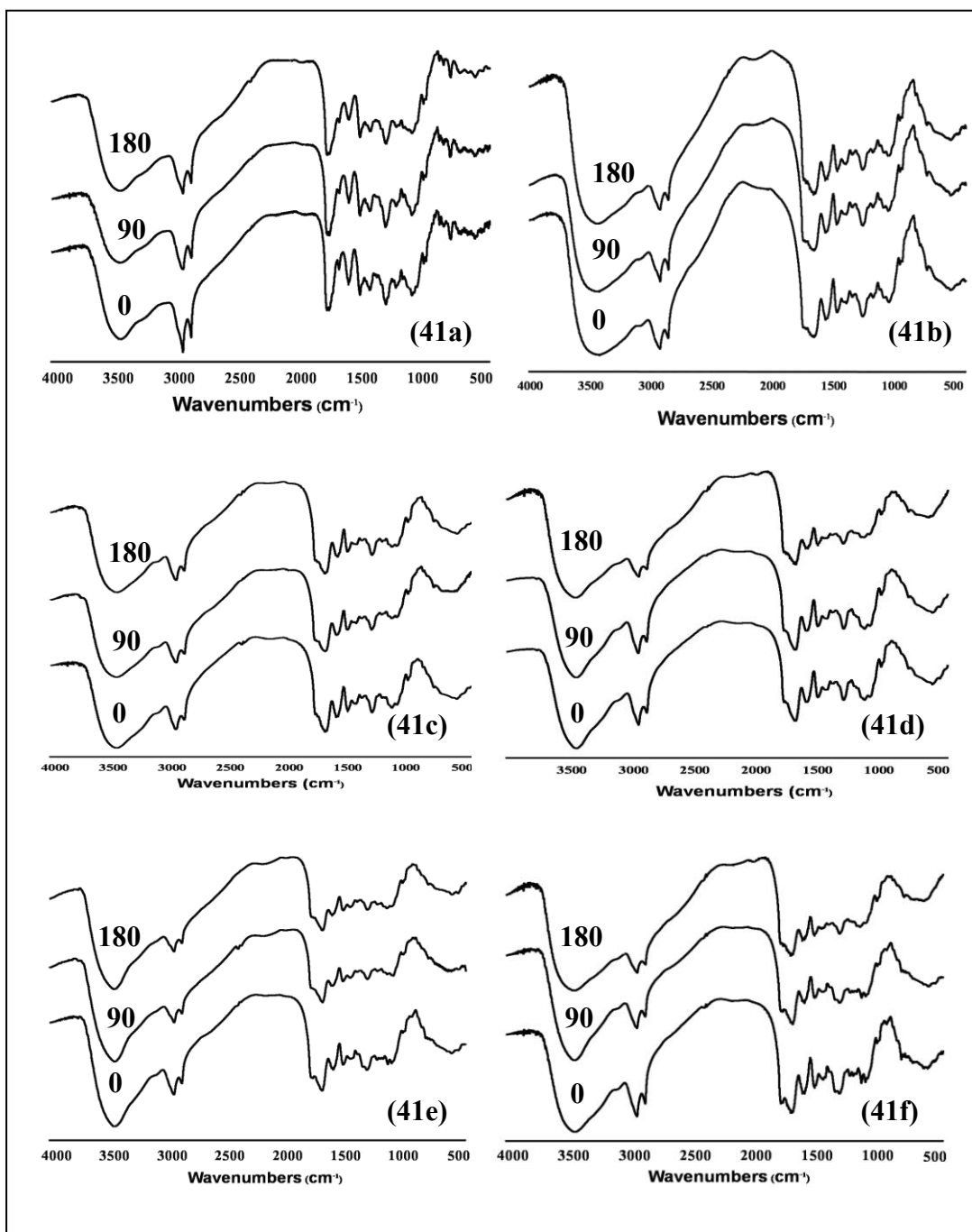


Figure 41 FTIR spectra of shellac (41a), unplasticized composite polymer film (41b) plasticized composite polymer films with PEG 400 5% (41c), PEG 400 10% (41d), DEP 5% (41e) and DEP 10% (41f) upon storage for 180 days at 40 °C, 75% RH

### 3.6 Acid value and percentage of insoluble solid

The aging of shellac was reported, because of the polymerization among hydroxyl groups and carboxyl groups, causing the instability of shellac (Specht 1998 : 20-28) which was predicted by two parameters i.e., acid value and percentage of insoluble solid as shown in Figures 42-43. Figure 42 shows the effect of types and concentrations of plasticizers on the acid value of composite polymer after 180 days of storage. Initially, the acid value of plasticized composite polymer was higher than the unplasticized film. The values were 76.00, 62.00, 68.48, 71.81, 63.98, 66.58 mgKOH/g sample for single shellac, unplasticized composite polymer and plasticized composite polymer with PEG 400 and DEP at 5 and 10%, respectively. The result was due to the reduction of electrostatic interaction between shellac and gelatin by the addition of plasticizer which was confirmed by the change in the FTIR spectra of plasticized composite polymer. Upon storage, the single shellac and the composite polymer with DEP at 5 and 10% was extremely decreased the acid value. It led to the higher polymerization whereas the composite polymer without plasticizers and with PEG 400 at 5 and 10% which indicated by the slight decrease in the acid value upon 180 days of storage, exhibiting the higher stability of film. The acid value of composite polymer film with DEP at 5% and 10% decreased from 63.98 to 52.17 mg KOH / g shellac and from 66.58 to 46.38 mg KOH / g shellac after 180 days of storage.

The reduction in acid value was related with the increase in the percent insoluble solid due to the esterification at the carboxylic and hydroxyl groups, leading to the instability of shellac. Upon storage, shellac was polymerized and the percentage of insoluble solid was formed. Figure 43 demonstrates the percent insoluble solid of shellac and gelatin composite polymers with and without plasticizers. The insoluble solid of shellac, unplasticized composite polymer, plasticized composite polymer with PEG 400 5% and 10% and with DEP 5 % and 10 % increased from 0.74%, 0.27%, 0.29%, 0.53%, 0.44% and 0.50% to 51.69 %, 1.61 %, 2.11 % 3.60 %, 7.24% and 12.89% , respectively upon 180 days of storage. The slight change was found for unplasticized and plasticized composite polymer with PEG 400 of both concentrations whereas the extreme increase ( $P < 0.01$ ) was shown for shellac and plasticized

composite polymer with DEP of both concentrations after 180 days of storage. The change in insoluble solid was in agreement with the change in the acid value.

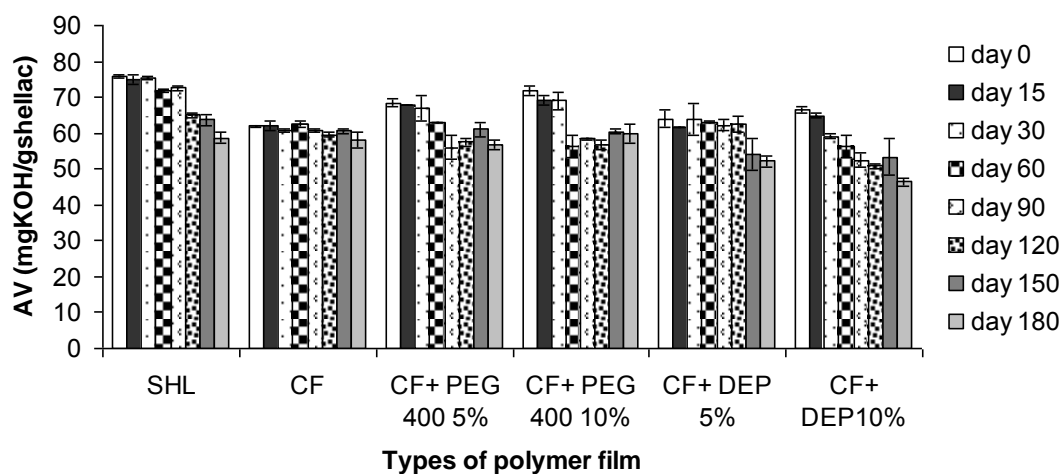


Figure 42 Effect of types and concentrations of plasticizers on acid value of composite polymer films based on shellac and gelatin upon storage for 180 days at 40 °C, 75% RH

The extent of reduction in the electrostatic interaction between shellac and gelatin, indicated by the different increase in the acid value and the change in FTIR spectra was dependent on type and concentration of plasticizer. The reduction of electrostatic interaction between shellac and gelatin attributed to the increase in the free carboxyl and hydroxyl group of shellac, causing the polymerization at these groups. The appropriate types and concentrations of plasticizers played an important role in this study. Between both plasticizers in this study, PEG 400 showed the slight effect on the increase in the percent insoluble solid of composite polymer at both concentrations 5 and 10% due to the ability of the hydrogen bonding formation of PEG between site chain of polymer, exhibiting the higher surface free energy and polarity of polymer films. The high polarity was due to the high OH group, contributing to the stronger hydrogen bonding within polymer chains network formed, leading to the lower polymerization. The result was in agreement with the other studies (Manee Luangtana-anan et al. 2007 : 687-692; Manee Luangtana-anan et al.

2010 : 12934-12940). The concentrations of PEG had slight influence on the stability of composite polymer, indicated by the lower percent insoluble solid upon storage for 180 days. However, the addition of DEP could not perform the protective capability efficiently of composite polymer films. As the higher concentrations of DEP, the higher polymerization of composite polymer was achieved, indicated by the higher percent insoluble solid and the lower acid value. The result was due to DEP had a lower polarity indicated by the lower surface free energy and percent polarity. It was attributed to the lower polar group giving the lower hydrogen bond between DEP and polymer chains and the difficulty in insertion between polymer networks due to the hydrophobic nature. In addition, DEP could be lost during the storage, leading to the higher polymerization. The loss of DEP was in agreement with other studies (Lin, Chen and Run-Chu, 2000: 343-350; Manee Luangtana-anan et al. 2007 : 687-692) and was related with the change in FTIR spectra of plasticized film. Therefore, PEG 400 at 5% and 10% was the plasticizer that could protect the composite polymer films from the polymerization process due to the polar groups and lower losing of plasticizers, attributing to the stability of composite polymer. The result was in agreement with other studies (Manee Luangtana-anan et al. 2007 : 687-692; Manee Luangtana-anan et al. 2010 : 12934-12940). Manee Luangtana-anan et al. found that the suitable plasticizer on the stability enhancement of shellac was due to the protection of plasticizer at active sites and hence the lower polymerization of shellac chain. PEG 400 was the only plasticizer that could protect at active sites whereas triacetin (TA) and diethyl phthalate (DEP) could not improve the stability of shellac, attributing to the lower molecular weight and the loss of plasticizers (Manee Luangtana-anan et al. 2007 : 687-692). Manee Luangtana-anan et al. reported that the different molecular weights of PEG had some influences on the stability of the shellac films. Among different molecular weights of PEG, PEG 400 showed the suitable molecular weight that could protect shellac chain at the carboxylic and hydroxyl groups (Manee Luangtana-anan et al. 2010 : 12934-12940). Therefore, the type and concentration of plasticizer played a crucial role for the protective ability at the active sites.

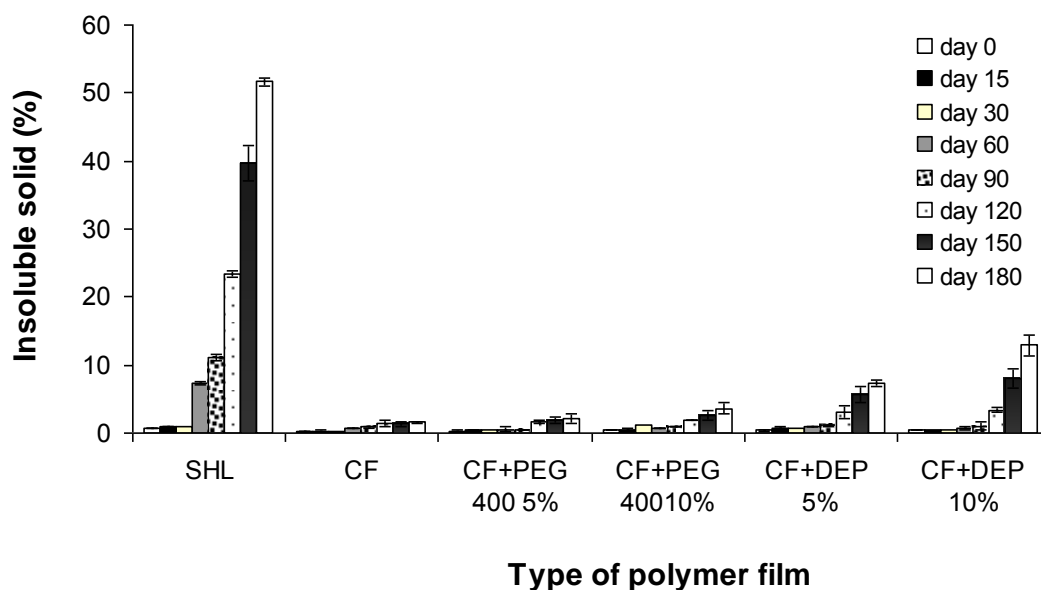


Figure 43 Effect of types and concentrations of plasticizers on percentage of insoluble solid of composite polymer films based on shellac and gelatin upon storage for 180 days at 40 °C, 75% RH

### 3.7 Summary

From the result could be concluded that the effect of type and concentration of plasticizer could apply to improve the stability of composite polymer in term of mechanical property upon storage for 180 days. The increased mechanical property of all plasticized composite polymer films was due to the hydrogen bonding formation between plasticizer and polymer chain network. PEG could form a stronger hydrogen bond rather than DEP upon storage. In addition, PEG 400 at both concentrations could also protect the polymerization at the active site of composite polymer chains by the hydrogen bonding under the longer period of storage whereas the addition of DEP could not perform the protective capability efficiently. Therefore, PEG 400 of both concentrations could be used for further investigation.

#### **4. Evaluation of shellac and gelatin composite polymer as edible film coating in food and pharmaceutical applications**

##### **4.1 Evaluation of film coating efficiency**

The work of adhesion and spreading coefficient was calculated based on the surface free energy values and was used to predict the potential of coating solution over the various substrates. Two types of substrates were investigated, glass and Teflon represented hydrophilic and hydrophobic model, respectively, indicated by either high total surface free energy or high percent polarity for hydrophilic surface and low total surface free energy or low percent polarity for hydrophobic surface. The values of the surface free energy and % polarity were 60.32 mN/m and 81.08 %, respectively for glass surface and 26.59 mN/m and 1.35%, respectively for Teflon surface were shown in Table 22. The effect of gelatin content on the work of adhesion and spreading coefficient of composite polymer solution over glass and Teflon surfaces was shown in Table 23. The higher gelatin content, the lower contact angle, the higher work of adhesion and spreading coefficient were obtained for the glass substrate. (The contact angle of film coating over glass and Teflon surface was shown in Appendix, Table 52). The work of adhesion and spreading coefficient value increased from 66.42 to 83.53 mN/m and from -8.14 to -3.07 mN/m as gelatin increased to 50% w/w, indicating the improvement of coating efficiency. The data was significantly changed ( $P < 0.01$ ). The increase in coating efficiency was due to the increase in hydrophilic nature of composite polymer as the higher gelatin content indicated by the higher surface free energy and percent polarity giving the higher attraction with glass surface and hence the high work of adhesion and spreading coefficient were obtained. Therefore, the result could prove that the coating potential of shellac over hydrophilic substrate could be modified by the addition of gelatin. However, for hydrophobic substrate, the opposite effect was also reported. The work of adhesion and spreading coefficient value decreased from 51.77 to 47.46 mN/m and from -22.79 to -39.14 mN/m as gelatin increased to 50%w/w, indicating the reduction of coating efficiency. This was the result of hydrophobic surface of Teflon having a low interaction with the hydrophilic composite polymer and hence lower work of adhesion and spreading coefficient were reported. Therefore, the incorporation of various concentrations of

gelatin could be used to modify the potential of coating of shellac and gelatin composite film over the coated substrate enabling to a wider range of application for coating in food and pharmaceutical industries.

Table 24 shows the effect of type and concentrations of plasticizers on work of adhesion and spreading coefficient of shellac and gelatin composite polymer solution over glass and Teflon. For the glass surface, the addition of polyethylene glycol and the increase in concentration gave the higher work of adhesion and the higher spreading coefficient due to the influence of hydrophilic nature of plasticizer giving the higher attraction with hydrophilic surface whereas the opposite effect was obtained for the incorporation of hydrophobic plasticizer, diethyl phthalate, and the increase in concentration of diethyl phthalate. For the Teflon surface showed the reduction in work of adhesion and spreading coefficient when the effect of polyethylene glycol and increased concentration was investigated whereas the opposite result was obtained for the addition of diethyl phthalate. The result could prove that the coating potential of shellac and gelatin composite polymer over hydrophilic substrate could be modified by the addition of hydrophilic plasticizers while the addition of hydrophobic plasticizer could enhance the efficiency of film coating over hydrophobic surface. Therefore, the application of type and concentration of plasticizer could be used to improve the coating efficiency of substrate depending on the hydrophobic and hydrophilic nature of substrate and plasticizer. The result obtained from the model substrate could be extrapolated to the coating efficiency of food and drug surface as explained in the following section.

Table 22 Total surface free energy and their component of glass and Teflon

Type of substrates	Surface free energy and their component			
	Total (mN/m)	Dispersive (mN/m)	Polar (mN/m)	Polarity (%)
Glass	60.32 ± 3.76	11.41 ± 2.87	48.91 ± 3.17	81.08
Teflon	26.59 ± 2.32	26.23 ± 2.90	0.36 ± 1.98	1.35

Table 23 Effect of gelatin content on work of adhesion and spreading coefficient of shellac and gelatin composite polymer solutions over glass and Teflon surface

Content of gelatin (% w/w)	Work of adhesion (mN/m)		Spreading coefficient (mN/m)	
	Glass	Teflon	Glass	Teflon
0	66.42±0.44	51.77± 0.89	-8.14± 0.44	-22.79± 0.89
10	72.08±0.87	51.54± 0.76	-6.12± 0.87	-26.66± 0.76
20	74.27±1.20	50.39± 3.04	-5.73± 1.20	-29.61± 3.04
30	77.11±0.76	50.27± 0.76	-4.55± 0.76	-31.39± 0.76
40	79.10±0.36	49.39±0.69	-3.44±0.36	-33.53±0.69
50	83.53±0.26	47.46± 3.36	-3.07±0.26	-39.14±3.36
100	92.99± 0.41	45.69±2.02	-1.49±0.41	-48.79±2.02

Table 24 Effect of types and concentrations of plasticizers on work of adhesion and spreading coefficient of shellac and gelatin composite polymer solutions over glass and Teflon surface

Content of gelatin (% w/w)	Work of adhesion (mN/m)		Spreading coefficient (mN/m)	
	Glass	Teflon	Glass	Teflon
SHL	66.42±0.44	51.77±0.89	-8.14±0.44	-22.79±0.89
CF	79.10±0.36	49.39±0.69	-3.44±0.36	-33.53±0.69
CF + PEG 400 5%	84.32±0.41	48.31±0.95	-3.30±0.35	-39.31±0.95
CF + PEG 400 10%	89.40±0.68	46.38±1.53	-2.92±0.68	-45.94±1.53
CF + DEP 5%	73.25±1.02	50.13±1.28	-5.41±1.02	-28.53±1.28
CF + DEP 10%	69.42±0.37	51.77±0.82	-6.50±0.37	-24.15±0.82

#### **4.2 Film coating efficiency of shellac and gelatin composite polymer as food application**

Edible film coating has been widely used in food and agro industries as prolongs the shelf life of fruits and vegetables. Therefore, the optimization of the composite polymer coating solutions on the ability to spread over a fruit skin can be evaluated. In this study banana and mango skin were chosen for coating study as its widely exported fruits. The components of forces of both skins were shown in Table 25. The % polarity of banana and mango are 6.74 and 5.06, indicating hydrophobic surface. The effect of gelatin content on the work of adhesion and spreading coefficient of composite polymer solution over banana and mango skin were shown in Table 26. The higher gelatin content, the higher contact angle, the lower work of adhesion and spreading coefficient were obtained for both fruit skins. (The contact angle of film coating over mango and banana skins was shown in Appendix, Table 53). The work of adhesion and spreading coefficient values decreased from 65.12 to 61.77 mN/m and from -9.44 to -24.82 mN/m for banana skin, respectively, and decreased from 61.95 to 59.28 mN/m and from -12.61 to -27.31 mN/m, respectively, for mango skin as gelatin increased to 50% w/w, indicating the reduction of coating efficiency due to the hydrophobic nature of fruit skins. The change in work of adhesion and spreading coefficient of both fruit skins was similar to the Teflon surface due to the hydrophobic surface. The hydrophobic of fruit skin resulted from the component of cell wall that consisted of cutin and wax, leading to the lower surface free energy and % polarity. In addition, the efficiency of film coating over fruit skins having a low interaction with the composite polymer at the higher concentrations of gelatin and hence lower work of adhesion and spreading coefficient were reported.

The effect of types and concentrations of plasticizers on the work of adhesion and spreading coefficient of shellac and gelatin composite polymer coating over banana and mango skin were shown in Table 27. The addition of polyethylene glycol attributed to the decrease in the coating efficiency of composite polymer solutions over all fruit skins indicated by the lower work of adhesion and spreading coefficient while diethyl phthalate showed the opposite trend. In addition, the higher

polyethylene glycol content, the higher contact angle, the lower work of adhesion and spreading coefficient were obtained for all fruit skins indicating the reduction in coating efficiency due to the hydrophobic of fruit skin having a low interaction with the hydrophilic polymer while the higher diethyl phthalate concentrations showed the opposite result. The result was in agreement with the Casariego et al. (Casariego et al. 2008: 1452-1459) and was similar result with the Teflon surface represented the hydrophobic substrate. Hence, the result could be concluded that the Teflon surface could be used as a model for hydrophobic substrate and could be extrapolated to the real surface skin in food industry.

Table 25 Total surface free energy and their component of banana and mango

Type of substrates	Surface free energy and their component			
	Total (mN/m)	Dispersive (mN/m)	Polar (mN/m)	Polarity (%)
Banana	31.01 ± 1.77	28.92 ± 1.26	2.09 ± 1.90	6.74
Mango	29.04 ± 0.80	27.57 ± 0.14	1.47 ± 0.13	5.06

Table 26 Effect of gelatin content on work of adhesion and spreading coefficient of shellac and gelatin composite polymer solutions over mango and banana skin

Content of gelatin (% w/w)	Work of adhesion (mN/m)		Spreading coefficient (mN/m)	
	Banana	Mango	Banana	Mango
0	65.12±0.53	61.95±0.60	-9.44±0.53	-12.61±0.60
10	64.99±0.70	61.42± 0.85	-13.21± 0.70	-16.78± 0.85
20	63.78±1.22	61.54± 0.91	-16.22± 1.22	-18.46± 0.91
30	62.67±1.35	60.53± 0.78	-18.99± 1.35	-21.13± 0.78
40	62.88±0.71	58.40±0.71	-20.04±0.71	-24.52±2.01
50	61.77±0.95	59.28± 0.72	-24.82±0.95	-27.31±0.72
100	56.92±0.94	56.26±2.13	-37.56±0.94	-38.22±2.13

Table 27 Effect of types and concentrations of plasticizers on work of adhesion and spreading coefficient of shellac and gelatin composite polymer solutions over mango and banana skin

Content of gelatin (% w/w)	Work of adhesion (mN/m)		Spreading coefficient (mN/m)	
	Banana	Mango	Banana	Mango
SHL	65.12±0.53	61.95±0.60	-9.44±0.53	-12.61±0.60
CF	62.88±0.71	58.40±0.71	-20.04±0.71	-24.52±2.01
CF + PEG 400 5%	62.45±1.56	57.38±4.12	-25.17±1.56	-30.24±4.12
CF + PEG 400 10%	61.10±3.21	54.74±0.49	-31.22±3.21	-37.58±0.49
CF + DEP 5%	66.98±0.35	62.12±0.62	-11.68±0.35	-16.54±0.62
CF + DEP 10%	67.34±0.65	64.98±1.99	-8.58±0.65	-10.94±0.42

#### 4.3 Film coating efficiency of shellac and gelatin composite polymer as pharmaceutical application

Two types of drugs was investigated, theophylline and aspirin represented basic and acidic drug model, respectively. The components of forces of both surfaces were shown in Table 28. The % polarity of theophylline and aspirin are 40.14 and 32.82 indicating hydrophilic surface. The effect of gelatin content on the work of adhesion and spreading coefficient of shellac and gelatin composite polymer solutions over drug tablets were shown in Table 29. The result showed that the higher gelatin content, the lower contact angle, the higher work of adhesion and spreading coefficient were obtained over two drug surface. (The contact angle of film coating over theophylline and aspirin tablet surface was shown in Appendix, Table 54). The work of adhesion and spreading coefficient values increased ( $P < 0.01$ ) from 53.17 to 78.92 mN/m and from -21.39 to -7.67 mN/m for theophylline tablet, respectively, and increased from 50.78 to 66.01 mN/m and from -23.78 to -20.58 mN/m, respectively, for aspirin tablet as gelatin increased to 50% w/w, indicating the improvement of coating efficiency. The drug surface showed the similar characteristic with the glass surface which represented hydrophilic surface. The increase in the coating efficiency was due to the increase in the hydrophilic nature of composite polymer as the higher

gelatin content giving the higher attraction with drug surface and hence the high work of adhesion and spreading coefficient were obtained. Therefore, the result could prove that the coating potential of shellac over hydrophilic substrate could be modified by the addition of gelatin.

The effect of types and concentrations of plasticizers on the work of adhesion and spreading coefficient of shellac and gelatin composite polymer solutions over drug tablets were shown in Table 31. The addition of polyethylene glycol attributed to the increase in coating efficiency of composite polymer solutions over two model drug tablets, indicated by the higher work of adhesion and spreading coefficient while diethyl phthalate showed the opposite trend. The higher polyethylene glycol concentrations, the lower contact angle, the higher work of adhesion and spreading coefficient were obtained over two drug model surfaces while the higher diethyl phthalate concentrations gave the opposite trend. The change in work of adhesion and spreading coefficient of all plasticized composite polymer solution over drug surface had a similar characteristic to the glass surface due to the hydrophilic surface. The increase in coating efficiency was due to the increase in hydrophilic nature of composite polymer as the higher hydrophilic plasticizer concentrations giving the higher attraction with drug surface and hence the high work of adhesion and spreading coefficient were obtained. The result could be concluded that the glass surface could be used as a model for hydrophilic substrate and could be extrapolated to the real surface skin in pharmaceutical industry.

Table 28 Total surface free energy and their component of theophylline and aspirin tablet

Type of substrates	Surface free energy and their component			
	Total (mN/m)	Dispersive (mN/m)	Polar (mN/m)	Polarity (%)
Theophylline	42.10 ± 2.55	25.20 ± 2.48	16.90 ± 2.01	40.14
Aspirin	39.89 ± 1.43	26.80 ± 1.90	13.09 ± 1.07	32.82

Table 29 Effect of gelatin content on work of adhesion and spreading coefficient of shellac and gelatin composite polymer solutions over theophylline and aspirin tablet

Content of gelatin (% w/w)	Work of adhesion (mN/m)		Spreading coefficient (mN/m)	
	Theophylline	Aspirin	Theophylline	Aspirin
0	53.17±2.48	50.78±1.03	-21.39±2.48	-23.78±1.03
10	61.65±1.92	54.85± 1.66	-17.15 ±1.92	-23.96 ± 1.66
20	66.33±0.83	55.79± 0.81	-12.40 ±0.83	-22.94 ± 0.81
30	71.18±0.44	58.98± 0.76	-10.87 ±0.44	-23.07 ± 0.76
40	74.44±0.92	61.58± 0.80	-8.48 ±0.92	-21.34 ± 0.80
50	78.92±0.71	66.01± 0.25	-7.67 ±0.71	-20.58 ± 0.25
100	91.02±1.00	82.10±1.35	-3.46±1.00	-12.38±1.35

Table 30 Effect of types and concentrations of plasticizers on work of adhesion and spreading coefficient of shellac and gelatin composite polymer solutions over theophylline and aspirin tablet

Content of gelatin (% w/w)	Work of adhesion (mN/m)		Spreading coefficient (mN/m)	
	Theophylline	Aspirin	Theophylline	Aspirin
SHL	53.17±2.48	50.78±1.03	-21.39±2.48	-23.78±1.03
CF	74.44±0.92	61.58±0.80	-8.48±0.92	-21.34±0.80
CF+PEG 400 5%	80.55±0.46	68.23±1.13	-7.07±0.46	-19.39±1.13
CF+PEG 400 10%	86.90±1.25	75.17±0.71	-5.42±1.25	-17.15±0.71
CF+DEP 5%	66.91±2.02	56.33±0.38	-11.75±2.02	-22.33±0.38
CF +DEP 10%	60.05±1.98	50.10±1.78	-15.87±1.18	-25.82±1.78

#### **4.4 Summary**

The result could prove that the coating potential of shellac over hydrophilic substrate could be modified by the addition of gelatin and hydrophilic plasticizer. This was the result of hydrophilic surface having a high interaction with the hydrophilic composite polymer due to the increased gelatin concentration and hence the higher work of adhesion and spreading coefficient were reported. However, the lower concentration of gelatin in the composite polymer and the addition of hydrophobic plasticizer could enhance the efficiency of film coating over hydrophobic surface. Hence, the proper type and concentration of plasticizer could be used to modify the potential of coating of shellac and gelatin composite polymer over the coated substrate enabling to a wider range of application for coating in food and pharmaceutical industries. Further study was to study the application of composite polymer as edible film coating for post harvest quality and prolong shelf of fruit product.

#### **5. Application of composite polymer as edible film coating for post harvest quality and prolonged shelf life of banana**

In this study was to investigate the efficiency of shellac and gelatin composite polymer as edible film coating for post harvest quality and extending the shelf life of tropical fruit product. The aging of all fruit was a result of various factors such as temperature, CO<sub>2</sub>, O<sub>2</sub>, and ethylene. The aging of fruit attributed to the change on substance and properties of fruit i.e., decreasing of chlorophyll, hydrolysis of starch, reduction of organic acid, oxidation of substrate, change in pectin form and cell wall softening (Phabha and Bhagyalaksmi 1998 : 915-920; Jingtare Siripanish 2006 : 75-101). Banana was chosen to study the efficiency of film coating to extending the shelf life on the longer period of storage. The stability of all banana coating samples was kept at 25 °C for 30 days. The composite polymer at 40% gelatin and polyethylene glycol 400 at 5% was chosen to further study the efficiency of edible film coating as post harvest quality and prolonged shelf life of banana under longer period of storage due to the higher mechanical properties, lower WVPC and higher stability. The composite polymer with and with out plasticizer were then

compared to single shellac and with out film coating. The change in the physicochemical properties such as color, titratable acidity, total soluble sugar (TSS), weight loss and firmness were also investigated as shown in Figure 44-49.

### 5.1 Color

The color is parameter to predict the aging of banana indicated by the color changed from green to yellow and to brown under the longer period of storage. Figure 44 shows the effect of different coating on color change of banana upon storage for 30 days. The result indicated that the color of uncoated banana was changed from green to yellow after storage only 10 days and further storage gave the extreme change in yellow color to brown color, while the banana coating with single shellac (S1), composite polymer (S2) and composite polymer with polyethylene glycol 400 (S3) did not change in color indicating the reduction in aging of banana. The degreening of all fruits was due to the degradation of chlorophyll which was degraded by enzyme chlorophyllase, attributing to the increase in other pigment such as carotene and xanthophyll (Phabha and Bhagyalaksmi 1998 : 915-920; Jingtare Siripanish 2006 : 75-101). Upon storage for 20 days, the brown color was formed for uncoated banana while the coated banana with all formulation showed the green/yellow color. The brown pigments was a result of the change in phenol to quinine by polyphenol oxidase (PPO) and increase in macromolecule by polymerization reaction, leading to the increase in brown pigment (Jingtare Siripanish 2006 : 75-101). The coated banana with S1, S2 and S3 formulation showed the slight change in the color due to the higher protection on moisture and the decrease in the respiration rate of banana, attributing to the lower change in chlorophyll of banana. Therefore, the result could prove that the coated banana with S2 and S3 could prolong the shelf life for 30 days when compared to S1 coating and without coating. The color change was confirmed by RGB image program as shown in Figure 45. The banana without coating showed the extreme decrease in all color i.e., red, green and blue upon storage for 10 days due to the aging of banana while the banana coating with S1, S2 and S3 was slightly decreased. The color of all samples tended to decrease as longer period time. However, the banana coating with S1, S2 and S3 could enhance the shelf life of banana upon storage for 30 days in comparison to S0.

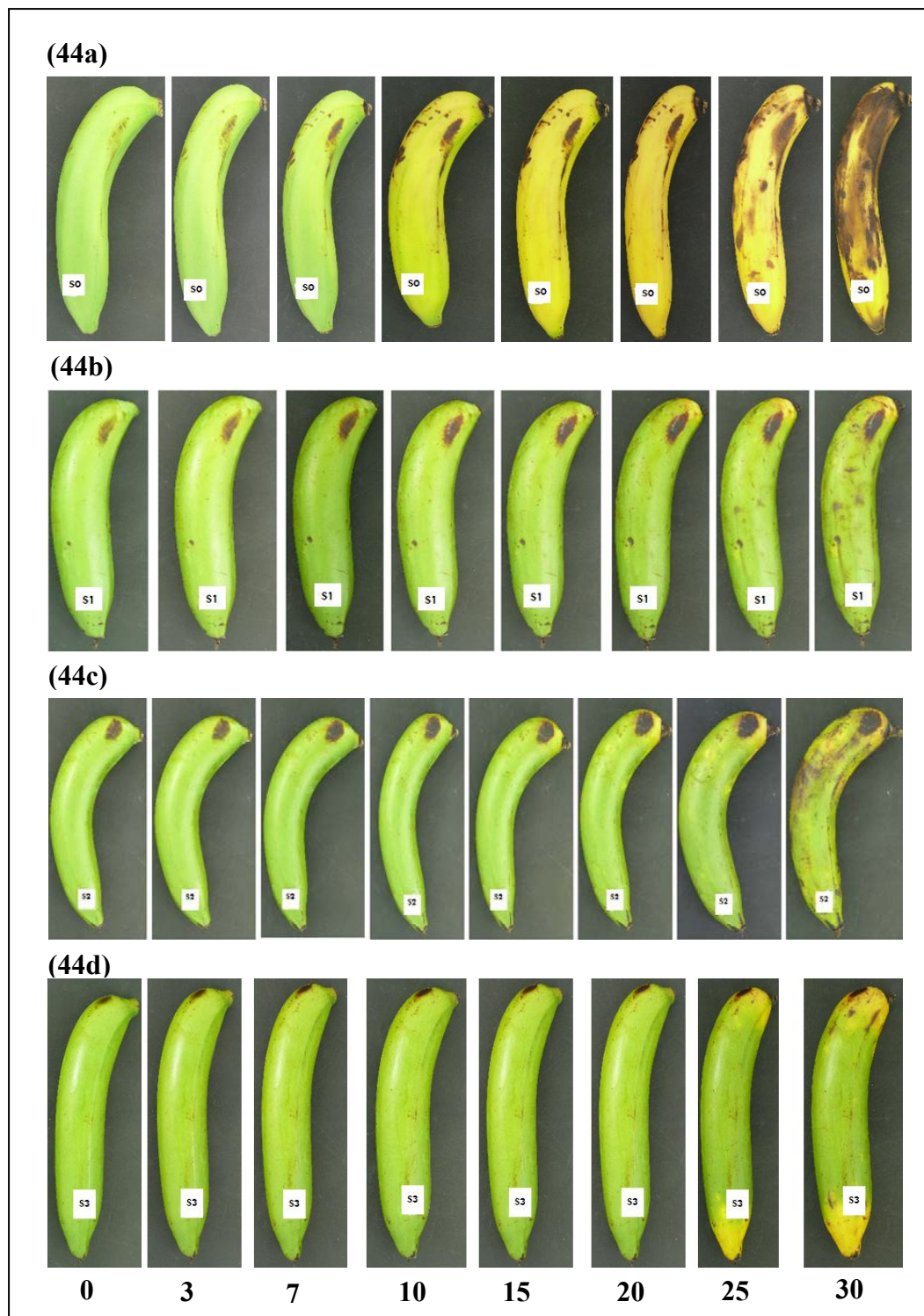


Figure 44 Effect of different film coating: without coating (44a, S0), coating with shellac (44b, S1), unplasticized composite polymer (44c, S2) and plasticized composite polymer with PEG 400 (44d, S3) on the color change of banana fruit upon storage at 25 °C for 30 days

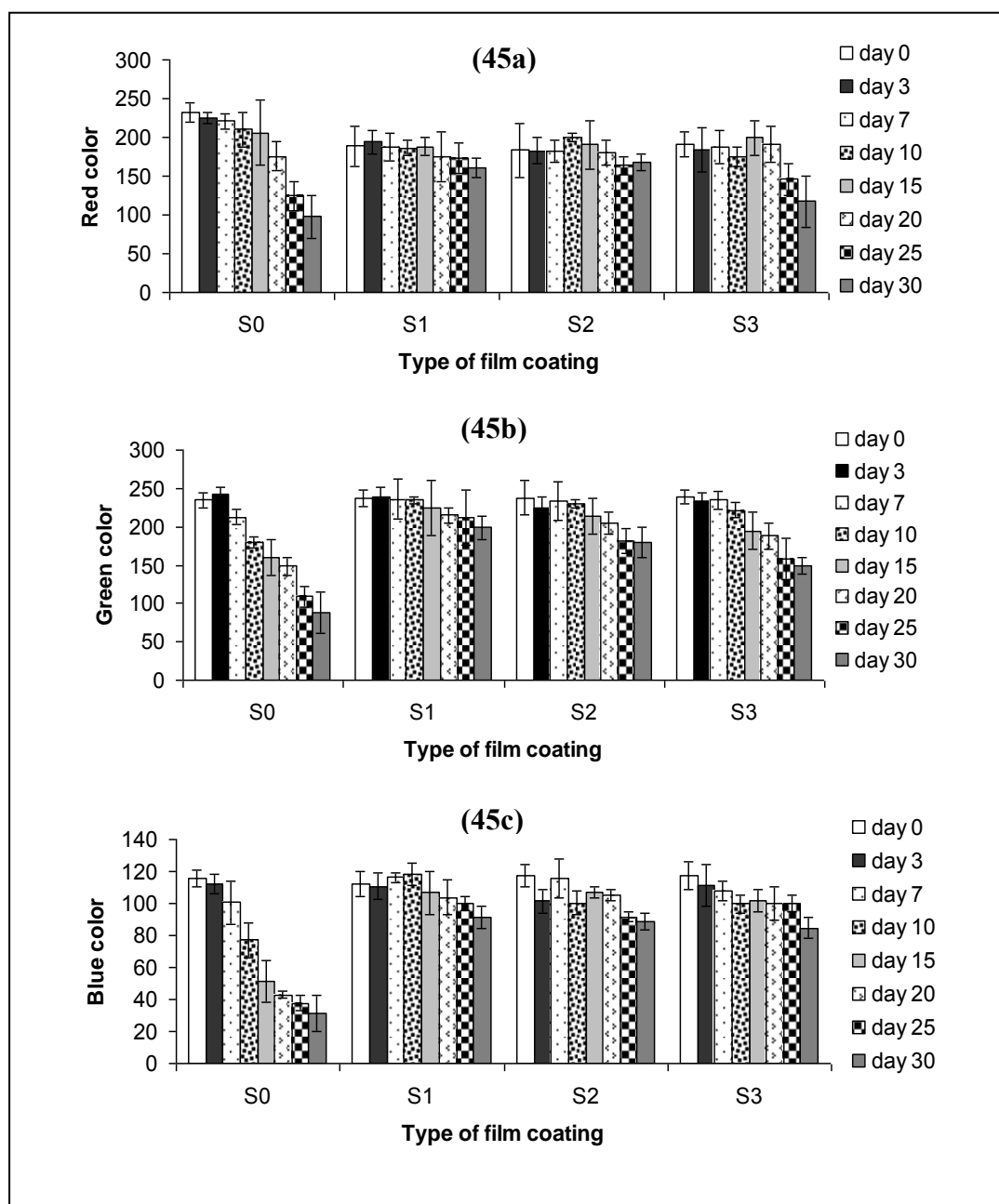


Figure 45 Effect of different film coating formulations on color obtained from RGB image program; red (45a), green (45b) and blue (45c) of banana upon storage at 25 °C for 30 days

## 5.2 Titratable acidity (TA)

The decrease in the respiration rate of all tropical fruit attributed to the lower change in the titratable acidity (TA) and total soluble sugars (TSS) (Bio et al. 2009). Figure 46 shows the effect of different coating on the TA of banana upon storage for 30 days. The TA of all banana samples was decreased ( $P < 0.01$ ) from 110.06, 104.87, 108.25 and 108.78 mg malic acid/100 g sample to 45.63, 76.38, 71.78 and 61.94 mg malic acid/100 g sample for S0, S1, S2 and S3 samples, respectively upon storage for 30 days. It was due to the change in the organic acids such as malic acid and citric acid, which were the prevalent organic acids in the banana fruit. It was used as substrates for the enzymatic reactions of respiration (Jingtare Siripanish, 2006 : 75-101; Bico et al. 2009 : 508-514). In general, the reduction of organic acid was due to the respiration of fruit within tricarboxylic cycle or the  $\text{CO}_2$  fixation at dark condition and deamination of amino acid (Pesis and Ben-Arie, 1986 : 644-648; Jingtare Siripanish, 2006 : 75-101; Bico et al. 2009 : 508-514). The TA of banana without coating was decreased more than the banana coating with S1, S2 and S3 indicating the coating of banana could enhance the shelf life of banana on longer period times. The decrease in TA was due to the aging of banana from the respiration and was related with the change in color.

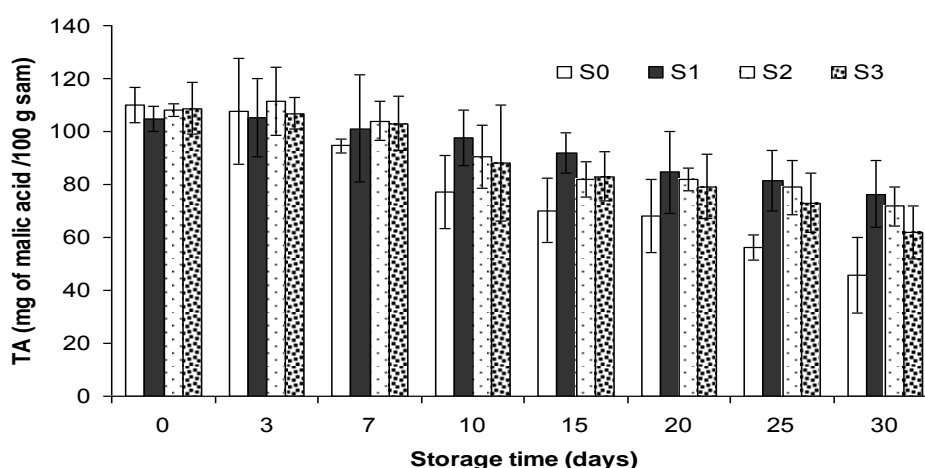


Figure 46 Effect of different film coating formulations on titratable acidity (TA) of banana upon storage at 25 °C for 30 days

### 5.3 Total soluble sugar (TSS)

The slight change in TA attributed to the lower % total soluble sugar (TSS) of banana fruit as shown in Figure 47. Initially, the % TSS of all banana samples with and without coating was in the range of 0.80-0.90 % w/w. The increase in % TSS was a result of the hydrolysis of starch and other carbohydrate. The total soluble sugar such as disaccharide i.e., sucrose and monosaccharides i.e., glucose and fructose were obtained from hydrolysis of starch and other carbohydrates (Phabha and Bhagyalaksmi 1998 : 915-920). Upon storage, the different change of banana fruit with and without coating was reported. The higher % TSS were obtained for banana without coating upon storage for 10 days while the samples as coating with S1, S2 and S3 formulation showed the lower % TSS. This result was due to the coating with S1, S2 and S3 could reduce the respiration rate of all banana fruit leading to the lower hydrolysis of starch. However, the banana samples with and without coating tended to increase in the % TSS under the longer storage time. At 30 days, the % TSS of all banana samples were increased from 0.88, 0.83, 0.85 and 0.80% to 20.45, 9.58, 10.33 and 13.72 % for S0, S1, S2 and S3 samples, respectively. The data was significantly changed ( $P < 0.01$ ). The increase in % TSS was related with the change in the color of banana fruit. Therefore, the result could be demonstrated that the banana coated with S1, S2 and S3 could be prolonged the shelf life of banana under the longer period for 30 days in comparison to S0.

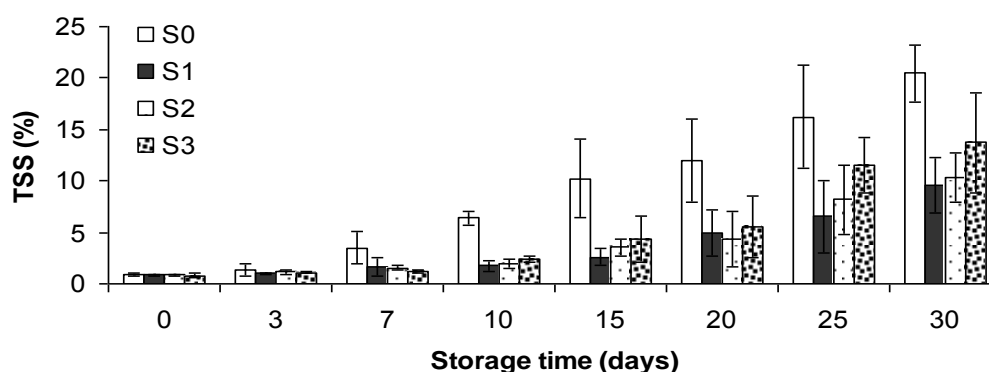


Figure 47 Effect of different film coating formulations on TSS of banana upon storage at 25 °C for 30 days

### 5.4 Weight loss

The weight loss of fruit was the factor predicting the quality of fruit due to the loss of water as shown in Figure 48. Initially, the lower change in the water loss was obtained of all banana samples and the values were 1.18, 0.83, 0.69, and 0.49 % w/w for S0, S1, S2 and S3 samples, respectively. Upon storage for 30 days, the control (S0) showed the highest of water loss (7.95%) while the coating of banana with S1, S2 and S3 indicated the lower water loss and the values were 4.78%, 5.26% and 5.10 %, respectively. The % weight loss of all banana samples at initial to 30 days of storage was significantly changed ( $P < 0.01$ ). The water loss was related with the change in color, TSS and TA and correlated with other reports (Pesis and Ben-Arie, 1986 : 644-648; Bico et al. 2009 : 508-514).

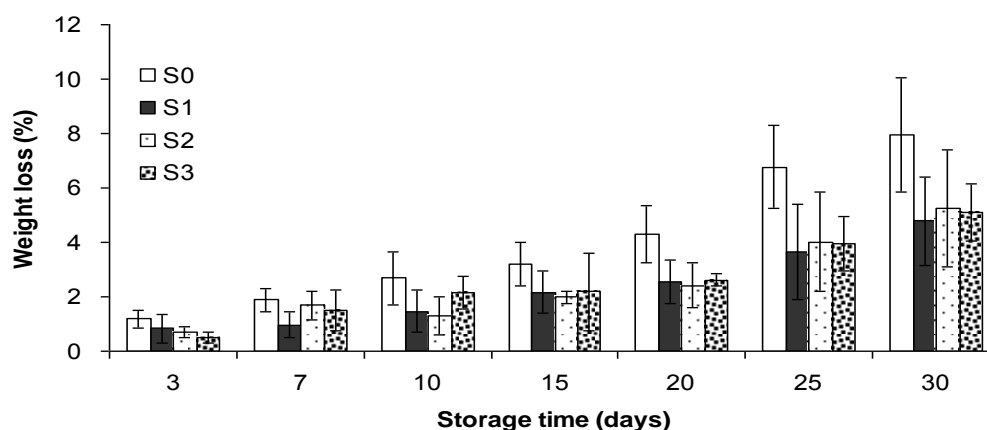


Figure 48 Effect of different film coating formulations on weight loss of banana storage at 25 °C for 30 days

### 5.5 Firmness

The change in water loss was associated with the decrease in the firmness of all banana samples as shown in Figure 49. Upon storage, all banana samples were decreased the firmness due to the loss of water and the aging of banana. The uncoating of banana was extremely decreased from 45.41 to 6.12 N, while the film coating with S1 decreased from 47.67 to 21.24 N, S2 decreased from 45.38 to 19.55 N and S3 decreased from 42.56 to 17.18 N, respectively upon storage for 30 days. The firmness of all banana samples at initial to 30 days of storage was

significantly changed ( $P < 0.01$ ). The reduction in the firmness represented the decrease in the hardness of skin due to the change in pectin at middle lamella of cell wall within banana skin. Initially, the fresh fruit consisted of pectin in term of protopectin which was insoluble in water. The aging of fruit led to the change in the protopectin form to pectin and pectic acid forms giving the solubility in water. The change from protopectin to pectin and pectic acid caused by depolymerization and desterification of pectin and polygalacturonase and pectinesterase was an enzyme to catalyze the reaction, attributing to softening of cell wall (Mc Collum et al. 1989 : 330-338; Toivonen and Brummell, 2008 : 1-14). Therefore, the film coating of all formulations could be prolonged the aging of banana upon storage for 30 days and was in agreement with the change in the %TSS, TA and % water loss of banana.

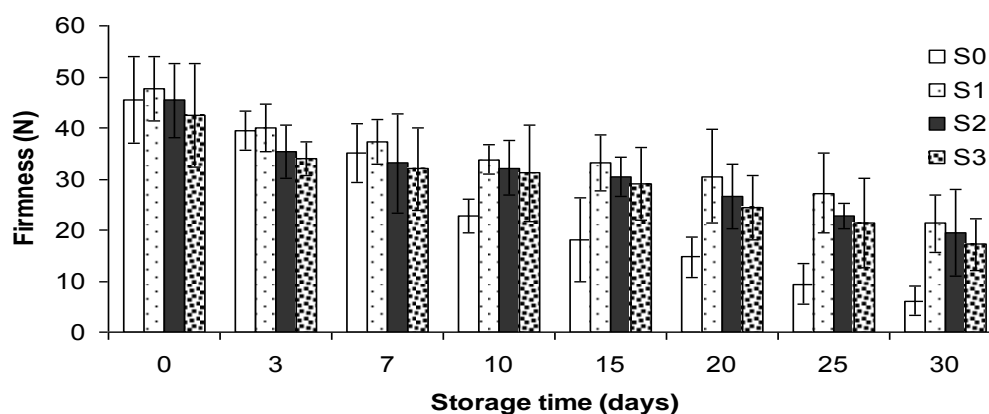


Figure 49 Effect of different film coating formulations on firmness of banana upon storage at 25 °C for 30 days

### 5.6 Summary

In conclusion, the formation of composite polymer with and without plasticizer as edible film coating could prolong the shelf life of banana under the longer period of storage for more than 30 days when compared to uncoated banana, indicated by the slow change in physicochemical properties of fruit such as color, titratable acidity (TA), total soluble sugar (TSS), weight loss and firmness. Hence, the coated food with the suitable composite polymer and plasticizer will be able to increase the value of exported food as longer times

## CHAPTER 5

### CONCLUSIONS

Edible film has been widely used in food and pharmaceutical industries and can be prepared from single or combination of biodegradable polymer. In this study, the attempt to prepare edible film by the formation of composite polymer between shellac and hydrophilic polymer was initiated since shellac, as a single film forming, has some drawbacks, i.e., the weak mechanical properties and instability. Gelatin was chosen as a hydrocolloid polymer to the formation of shellac and gelatin composite polymer due to an excellent film forming, good mechanical properties and plasticity. The composite polymer between shellac and gelatin could be formed by the electrostatic interaction between negative charge ( $\text{COO}^-$ ) from shellac and positive charge ( $\text{NH}_3^+$ ) from gelatin. The composite polymer exhibited the higher wettability, surface free energy and polarity as the increase in gelatin content, indicating the increase in hydrophilicity. The higher hydrophilicity attributed to the increase in water solubility, water content, water uptake, moisture sorption isotherm, water vapor permeability and mechanical properties. In addition, the modification of shellac by the formation of composite polymer with gelatin could not only enhance the mechanical properties but also reduce the polymerization of shellac. It was due to the insertion of gelatin within shellac network could protect the polymer chains of shellac from the cross linking formation of the esterification process. Therefore, it could be concluded that the polymerization of shellac could be protected by the electrostatic interaction between carboxyl and hydroxyl groups from shellac amino and carboxyl groups from gelatin. Hence, the attempt to improve the drawback of shellac by the formation of composite polymer between shellac and gelatin could be achieved. However, the modification of shellac by the formation of composite polymer with gelatin could not prolong the stability in term of mechanical properties for 180 days of storage, resulting from the loss of free water. Further investigation was required to improve the stability in term of mechanical properties of composite polymer film as the longer storage by adding plasticizer.

In this study, 40% gelatin was an appropriate concentration for further study of the effect of types and concentrations of plasticizers on the mechanical properties and stability of composite polymer film since 30 % gelatin showed a lower stabilized effect and 50% gelatin showed the higher WVPC giving the lower protection. The addition of PEG and DEP at 5 and 10% w/w could improve the stability of composite polymer in term of mechanical properties upon storage for 180 days but it had an influence on the stability in term of percentage of insoluble solid. It was due to the reduction of electrostatic interaction between shellac and gelatin, attributing to the increase in free carboxyl groups and hydroxyl groups, leading to the polymerization at the active sites of composite polymer film. However, the functional groups of plasticizer could protect the polymerization at the active site of composite polymer chains by the hydrogen bonding under the longer period of storage. Among plasticizers, PEG 400 showed the slight increase in the percent insoluble solid of composite polymer for both concentrations (5% and 10%) as a result of the ability of the hydrogen bonding formation of PEG between site chains of composite polymers whereas the addition of DEP could not perform the protective capability. As the higher concentration of DEP, the higher polymerization of composite polymer was observed. It was due to the lower hydrogen bonding between DEP and polymer chains as a result of low polarity and the difficulty in insertion between polymer networks and the higher loss of DEP due to the lower Mw upon storage for 180 days, leading to the higher polymerization. Therefore, PEG 400 of both concentrations could be applied to improve the mechanical properties of composite polymer film based on shellac and gelatin under the longer period of storage.

Glass and Teflon surface could be used as a model of hydrophilic and hydrophobic surface, respectively to preliminary predict the coating potential of food and pharmaceutical surfaces. The coating potential of shellac over hydrophilic substrate could be modified by the addition of gelatin and hydrophilic plasticizer. However, the lower concentration of gelatin in composite polymer and the addition of higher concentration of hydrophobic plasticizer could enhance the efficiency of film coating over hydrophobic surface. Hence, the proper type and concentration of plasticizer could be used to modify the potential of coating of shellac and gelatin

composite film over the coated substrate enabling to a wider range of application for coating in food and pharmaceutical industries.

The application of composite polymer with and without plasticizer as banana coating could enhance the shelf life upon storage more than 30 days indicated by the slow change in color, firmness, TSS and titratable acidity of fruit. The aging of fruit was a result of CO<sub>2</sub>, O<sub>2</sub> and ethylene and temperature, attributing to the aging of chlorophyll, hydrolysis of starch, the decrease in organic acid, the change in pectin form and cell wall softening, leading to the increase in pigment, sugar and respiration rate of fruit. The coated food with proper composite polymer and plasticizer will be able to add the value of exported food.

Therefore, the knowledge of composite polymer based on shellac and gelatin could contribute to the benefit of the research work and various applications for edible film coating in food and pharmaceutical industries.

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## **APPENDIX**

Table 31 Zeta potential, size, pH and viscosity of shellac and gelatin composite polymer film solutions

<b>Content of gelatin (%w/w)</b>	<b>Zeta potential (mV)</b>	<b>Size (<math>\mu\text{m}</math>)</b>
0	$-85.23 \pm 3.59$	$12.76 \pm 2.30$
10	$-71.20 \pm 3.18$	$15.40 \pm 1.95$
20	$-63.73 \pm 2.22$	$16.89 \pm 3.53$
30	$-56.42 \pm 1.83$	$21.52 \pm 2.92$
40	$-47.02 \pm 1.90$	$37.42 \pm 4.99$
50	$-40.09 \pm 4.87$	$42.54 \pm 2.90$
100	$5.49 \pm 0.09$	$6.63 \pm 0.76$

<b>Content of gelatin (%w/w)</b>	<b>pH</b>	<b>Viscosity (MPas)</b>
0	$8.14 \pm 0.06$	$0.74 \pm 0.05$
10	$8.02 \pm 0.01$	$0.90 \pm 0.08$
20	$7.96 \pm 0.02$	$1.46 \pm 0.10$
30	$7.89 \pm 0.03$	$5.04 \pm 1.29$
40	$7.81 \pm 0.02$	$14.25 \pm 1.52$
50	$7.79 \pm 0.02$	$23.59 \pm 3.94$
100	$5.42 \pm 0.04$	$2.92 \pm 0.51$

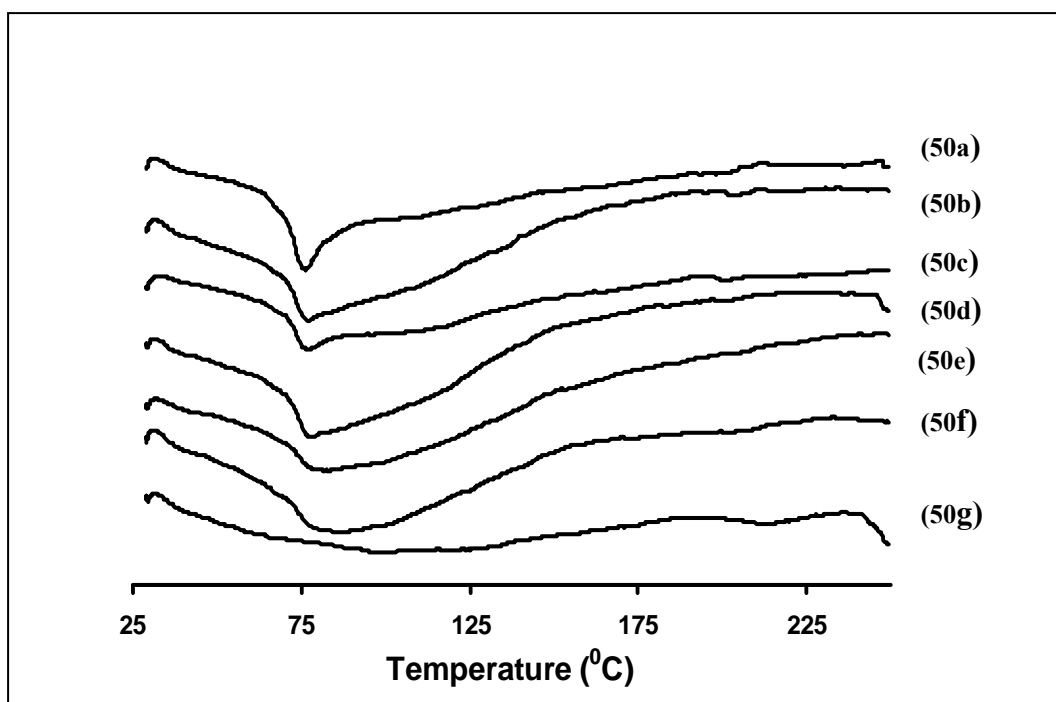


Figure 50 DTA thermogram of shellac (50a), shellac and gelatin composite polymers with various concentrations of gelatin %w/w: 10 (50b), 20 (50c), 30 (50d), 40 (50e), 50 (50f) and gelatin (50g)

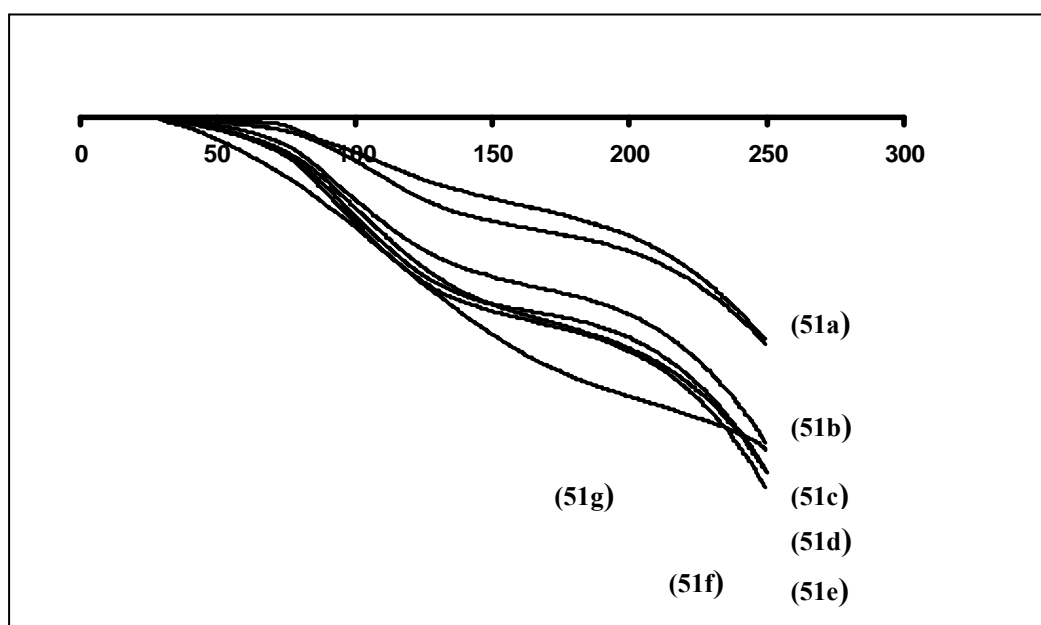


Figure 51 TG thermogram of shellac (51a), shellac and gelatin composite polymers with various concentrations of gelatin %w/w: 10 (51b), 20 (51c), 30 (51d), 40 (51e), 50 (51f) and gelatin (51g)

Table 32 Puncture strength of shellac and gelatin composite polymer film upon storage for 180 days at 40 °C, 75 % RH

Content of gelatin (% w/w)	Puncture strength (MPa)			
	day 0	day 15	day 30	day 60
0	3.61 ± 0.90	0.51 ± 0.13	0.54 ± 0.23	0.97 ± 0.35
10	5.01 ± 1.35	4.46 ± 1.89	1.26 ± 0.98	0.36 ± 0.06
20	8.51 ± 2.44	8.17 ± 4.70	0.97 ± 0.38	0.64 ± 0.17
30	11.83 ± 0.73	6.85 ± 3.73	5.75 ± 1.25	0.42 ± 0.07
40	14.07 ± 3.20	17.56 ± 5.07	13.25 ± 6.36	5.16 ± 2.03
50	15.58 ± 3.40	12.39 ± 2.73	13.15 ± 5.11	6.16 ± 1.33
100	23.18 ± 3.34	22.25 ± 6.36	17.56 ± 5.07	25.16 ± 7.03

Content of gelatin (% w/w)	Puncture strength (MPa)			
	day 90	day 120	day 150	day 180
0	0.68 ± 0.13	0.47 ± 0.10	0.39 ± 0.17	0.29 ± 0.07
10	0.66 ± 0.17	0.37 ± 0.18	0.31 ± 0.11	0.21 ± 0.11
20	0.85 ± 0.21	0.60 ± 0.18	0.45 ± 0.15	0.35 ± 0.12
30	0.77 ± 0.18	0.46 ± 0.11	0.93 ± 0.59	0.81 ± 0.52
40	1.27 ± 0.87	0.52 ± 0.32	0.54 ± 0.12	0.44 ± 0.22
50	1.31 ± 0.56	0.66 ± 0.12	0.61 ± 0.27	0.54 ± 0.13
100	19.27 ± 5.87	18.52 ± 4.42	20.54 ± 3.12	16.9 ± 2.09

Table 33 Percentage of elongation of shellac and gelatin composite polymer film upon storage for 180 days at 40 °C, 75 % RH

Content of gelatin (% w/w)	Elongation (%)			
	day 0	day 15	day 30	day 60
0	3.80 ±1.35	1.35 ±0.48	0.60 ± 0.27	1.10 ± 0.73
10	6.51 ±2.30	5.21 ±2.32	2.03 ± 1.88	1.75 ± 0.84
20	12.89 ±3.01	21.14 ±8.07	6.99 ± 4.20	1.14 ± 1.12
30	19.65 ±4.45	21.58 ±6.06	6.05 ± 3.64	0.67 ± 0.42
40	26.66 ±4.77	40.16 ±8.32	23.85 ±7.41	4.62 ± 2.93
50	32.47 ±8.42	41.61 ±4.51	21.85 ± 8.29	4.92 ± 1.13
100	38.23 ±3.40	43.85 ±15.41	40.16 ± 8.32	34.62 ± 2.93

Content of gelatin (% w/w)	Elongation (%)			
	day 90	day 120	day 150	day 180
0	1.69 ± 0.52	0.51 ± 0.25	1.08 ± 0.58	1.08 ± 0.26
10	1.02 ± 0.17	0.68 ± 0.37	1.09 ± 0.44	1.09 ± 0.14
20	1.74 ± 1.09	1.36 ± 0.46	0.67 ± 0.26	0.67 ± 0.35
30	1.28 ± 1.06	1.29 ± 0.98	0.84 ± 0.48	0.84 ± 0.28
40	2.72 ± 1.36	2.11 ± 0.71	0.52 ± 0.49	0.52 ± 0.15
50	2.86 ± 1.18	3.56 ± 0.53	0.72 ± 0.69	0.84 ± 0.25
100	22.72 ± 7.36	28.11 ± 5.71	25.52 ± 8.49	28.01 ± 6.89

Table 34 Acid value of shellac and gelatin composite polymer film upon storage for 180 days at 40 °C, 75 % RH

Content of gelatin (% w/w)	AV (mgKOH/g shellac)			
	day 0	day 15	day 30	day 60
0	76.00 ± 0.43	74.75 ± 1.34	75.30 ± 0.57	71.88 ± 0.40
10	70.65 ± 2.12	66.67 ± 1.10	63.12 ± 3.14	60.97 ± 1.17
20	67.56 ± 3.14	63.39 ± 0.56	62.84 ± 0.08	61.62 ± 1.81
30	64.43 ± 0.76	62.42 ± 1.94	61.47 ± 1.98	62.05 ± 2.63
40	62.00 ± 0.18	62.02 ± 1.37	60.53 ± 0.44	62.47 ± 0.88
50	57.36 ± 0.69	60.29 ± 1.64	60.00 ± 1.23	57.99 ± 1.58
100	NA*	NA*	NA*	NA*

Content of gelatin (% w/w)	AV (mgKOH/g shellac)			
	day 90	day 120	day 150	day 180
0	72.19 ± 0.00	65.08 ± 0.69	63.72 ± 1.63	58.73 ± 1.65
10	62.76 ± 2.64	59.90 ± 0.35	61.02 ± 1.60	56.53 ± 0.35
20	57.53 ± 2.40	57.13 ± 1.55	57.48 ± 3.46	54.90 ± 0.96
30	62.01 ± 0.93	59.49 ± 0.57	58.92 ± 0.35	57.51 ± 2.02
40	60.59 ± 0.42	59.63 ± 0.71	60.60 ± 0.67	58.18 ± 2.14
50	58.49 ± 2.00	58.68 ± 0.70	57.38 ± 0.72	54.18 ± 0.69
100	NA*	NA*	NA*	NA*

\*Data cannot measure in this study

Table 35 Insoluble solid of shellac and gelatin composite polymer film upon storage for 180 days at 40 °C, 75 % RH

Content of gelatin (% w/w)	IS (%)			
	day 0	day 15	day30	day 60
0	0.74 ± 0.04	0.93 ± 0.06	1.04 ± 0.29	3.82 ± 0.38
10	0.64 ± 0.03	0.44 ± 0.20	0.55 ± 0.11	2.88 ± 0.76
20	0.50 ± 0.01	0.48 ± 0.02	0.95 ± 0.07	2.81 ± 0.03
30	0.56 ± 0.01	0.55 ± 0.07	0.90 ± 0.36	1.19 ± 0.18
40	0.44 ± 0.10	0.39 ± 0.23	0.54 ± 0.06	1.11 ± 0.10
50	0.67 ± 0.38	0.34 ± 0.15	0.58 ± 0.21	1.01 ± 0.11
100	0.01 ± 0.00	0.00 ± 0.00	0.01 ± 0.00	0.01 ± 0.00

Content of gelatin (% w/w)	IS (%)			
	day 90	day 120	day 150	day 180
0	11.18 ± 0.46	23.40 ± 0.39	39.77 ± 2.59	51.69 ± 0.63
10	5.13 ± 0.44	15.63 ± 2.55	25.31 ± 2.37	45.28 ± 1.46
20	2.56 ± 0.23	6.08 ± 1.55	22.65 ± 1.21	23.83 ± 2.03
30	1.02 ± 0.33	4.15 ± 1.01	4.27 ± 0.97	6.02 ± 0.93
40	0.86 ± 0.17	1.37 ± 0.50	1.31 ± 0.34	1.61 ± 0.08
50	0.75 ± 0.03	1.23 ± 0.08	1.14 ± 0.14	1.55 ± 0.01
100	0.02 ± 0.00	0.00 ± 0.00	0.01 ± 0.00	0.03 ± 0.00

Table 36 WVPC of shellac and gelatin composite polymer film upon storage for 180 days at 40 °C, 75 % RH

Content of gelatin (% w/w)	WVPC x 10 <sup>-8</sup> gh <sup>-1</sup> m <sup>-1</sup> Pa <sup>-1</sup>		
	day 0	day 90	day 180
0	4.15 ± 0.16	2.49 ± 0.62	1.29 ± 0.41
10	4.43 ± 0.61	1.94 ± 0.81	2.95 ± 1.34
20	4.92 ± 0.19	3.88 ± 1.19	2.66 ± 0.45
30	5.34 ± 0.51	3.41 ± 0.67	2.49 ± 1.69
40	6.12 ± 0.80	4.35 ± 1.38	2.00 ± 0.32
50	9.46 ± 0.46	3.79 ± 1.82	4.74 ± 0.41
100	12.15 ± 2.90	11.49 ± 3.87	10.29 ± 3.09

Table 37 Moisture content of shellac and gelatin composite polymer film upon storage for 180 days at 40 °C, 75 % RH

Content of gelatin (% w/w)	Moisture content (%)		
	day 0	day 90	day 180
0	8.61 ± 1.00	7.77 ± 0.36	5.03 ± 1.44
10	9.56 ± 0.23	8.57 ± 0.95	5.12 ± 1.42
20	10.10 ± 0.71	7.20 ± 1.41	5.95 ± 0.91
30	10.62 ± 0.52	7.12 ± 0.09	5.57 ± 0.83
40	12.46 ± 0.28	9.26 ± 0.29	6.23 ± 1.13
50	12.74 ± 0.21	9.23 ± 0.16	6.66 ± 0.84
100	14.54 ± 2.89	13.90 ± 3.46	13.06 ± 1.87

Table 38 Wettability of shellac and gelatin composite polymer film (distilled water) upon storage for 180 days at 40 °C, 75 % RH

Content of gelatin (% w/w)	Contact angle (degree)		
	day 0	day 90	day 180
0	81.39 ± 1.32	83.34 ± 3.30	92.01 ± 1.18
10	78.15 ± 1.29	80.35 ± 2.64	84.59 ± 2.35
20	75.91 ± 2.04	79.23 ± 2.33	80.83 ± 1.37
30	73.97 ± 1.10	77.01 ± 1.57	79.19 ± 0.24
40	70.89 ± 0.72	75.61 ± 0.89	76.50 ± 1.20
50	68.55 ± 0.57	73.69 ± 3.33	75.09 ± 4.11
100	64.12 ± 3.40	65.09 ± 15.41	68.14 ± 3.32

Table 39 Wettability of shellac and gelatin composite polymer film (formamide) upon storage for 180 days at 40 °C, 75 % RH

Content of gelatin (% w/w)	Contact angle (degree)		
	day 0	day 90	day 180
0	57.72 ± 0.68	65.35 ± 5.01	69.35 ± 5.01
10	53.68 ± 2.04	59.04 ± 1.67	64.07 ± 2.44
20	51.73 ± 1.32	57.63 ± 2.11	59.96 ± 3.14
30	49.35 ± 0.60	55.42 ± 2.24	58.98 ± 1.84
40	48.95 ± 1.08	54.78 ± 2.57	57.56 ± 1.57
50	45.48 ± 1.32	55.46 ± 3.24	57.53 ± 2.33
100	38.23 ± 2.70	40.85 ± 3.01	42.16 ± 2.18

Table 40 Wettability of shellac and gelatin composite polymer film (diiodomethane) upon storage for 180 days at 40 °C, 75 % RH

Content of gelatin (% w/w)	Contact angle (degree)		
	day 0	day 90	day 180
0	62.87 ± 1.96	59.87 ± 2.05	55.54 ± 3.14
10	63.70 ± 1.01	57.72 ± 2.31	53.21 ± 2.04
20	64.97 ± 2.56	56.97 ± 3.48	54.74 ± 4.48
30	68.74 ± 1.02	56.46 ± 1.94	55.13 ± 1.57
40	71.30 ± 5.28	59.15 ± 2.28	56.24 ± 3.37
50	73.10 ± 1.29	58.09 ± 3.20	56.91 ± 2.51
100	75.06 ± 2.89	64.75 ± 0.41	63.06 ± 3.12

Table 41 Surface free energy of shellac and gelatin composite polymer film upon storage for 180 days at 40 °C, 75 % RH

Content of gelatin (% w/w)	Surface free energy (mN/m)		
	day 0	day 90	day 180
0	37.28 ± 1.96	34.96 ± 3.96	34.32 ± 4.05
10	39.10 ± 1.01	37.47 ± 3.57	37.33 ± 4.51
20	40.00 ± 2.56	38.56 ± 3.33	38.07 ± 3.97
30	40.83 ± 1.02	39.49 ± 2.74	38.53 ± 4.01
40	41.46 ± 1.28	39.61 ± 2.79	38.84 ± 3.37
50	43.30 ± 1.29	40.26 ± 3.72	40.04 ± 3.83
100	47.24 ± 1.87	46.12 ± 0.50	45.10 ± 0.44

Table 42 Polarity of shellac and gelatin composite polymer film upon storage for 180 days at 40 °C, 75 % RH

Content of gelatin (% w/w)	Polarity (%)		
	day 0	day 90	day 180
0	26.23 ± 5.33	25.66 ± 3.52	14.98 ± 5.86
10	29.39 ± 3.47	25.33 ± 6.89	24.11 ± 4.21
20	31.88 ± 2.84	26.82 ± 5.98	24.95 ± 4.50
30	35.66 ± 0.11	29.17 ± 6.06	26.42 ± 5.50
40	39.85 ± 4.77	29.59 ± 4.55	28.17 ± 5.09
50	42.82 ± 2.34	30.35 ± 7.01	27.52 ± 4.00
100	46.16 ± 5.83	39.27 ± 1.50	36.13 ± 1.30

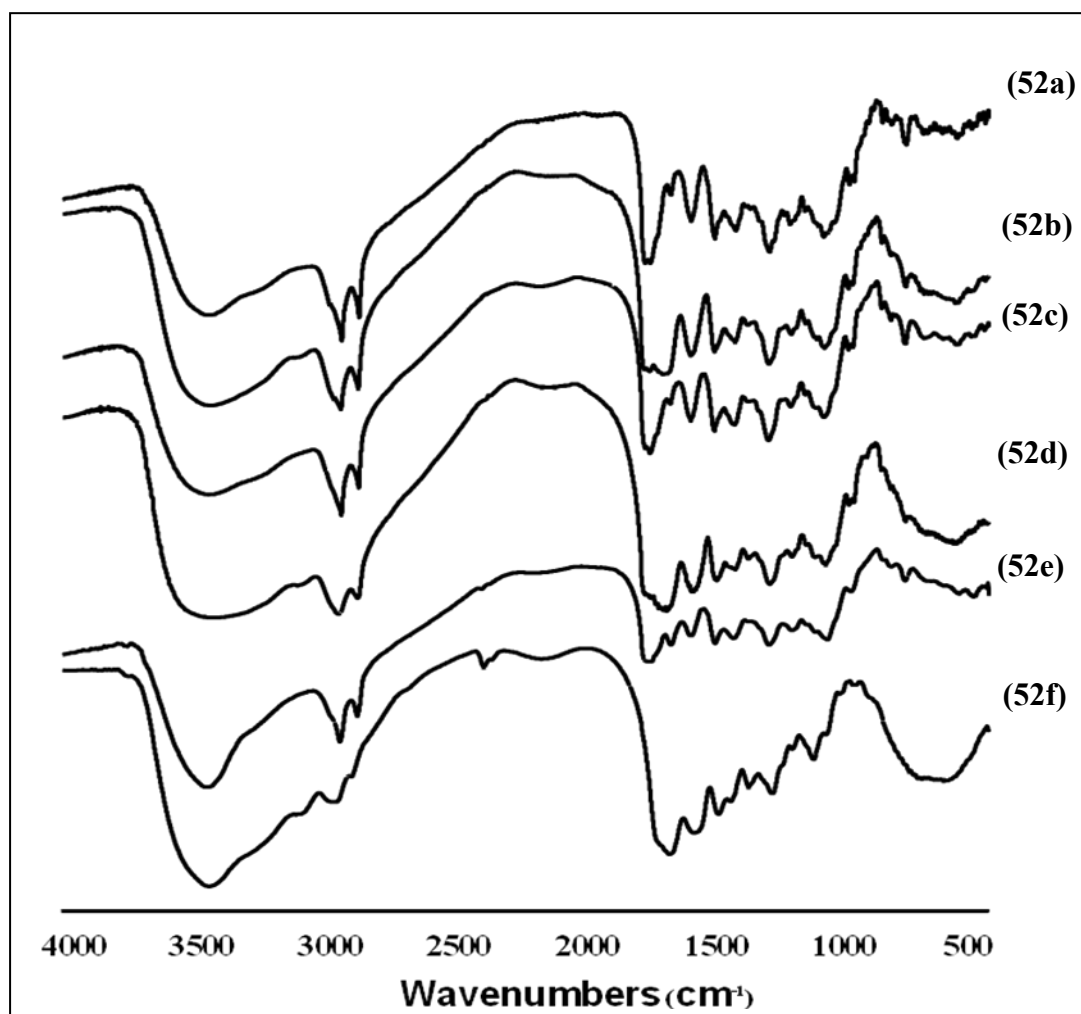


Figure 52 FTIR spectroscopy of single shellac (52a), shellac and gelatin composite polymers and physical mixture with low gelatin (52b, 52c) and high gelatin (52d, 52e) and single gelatin (52f)

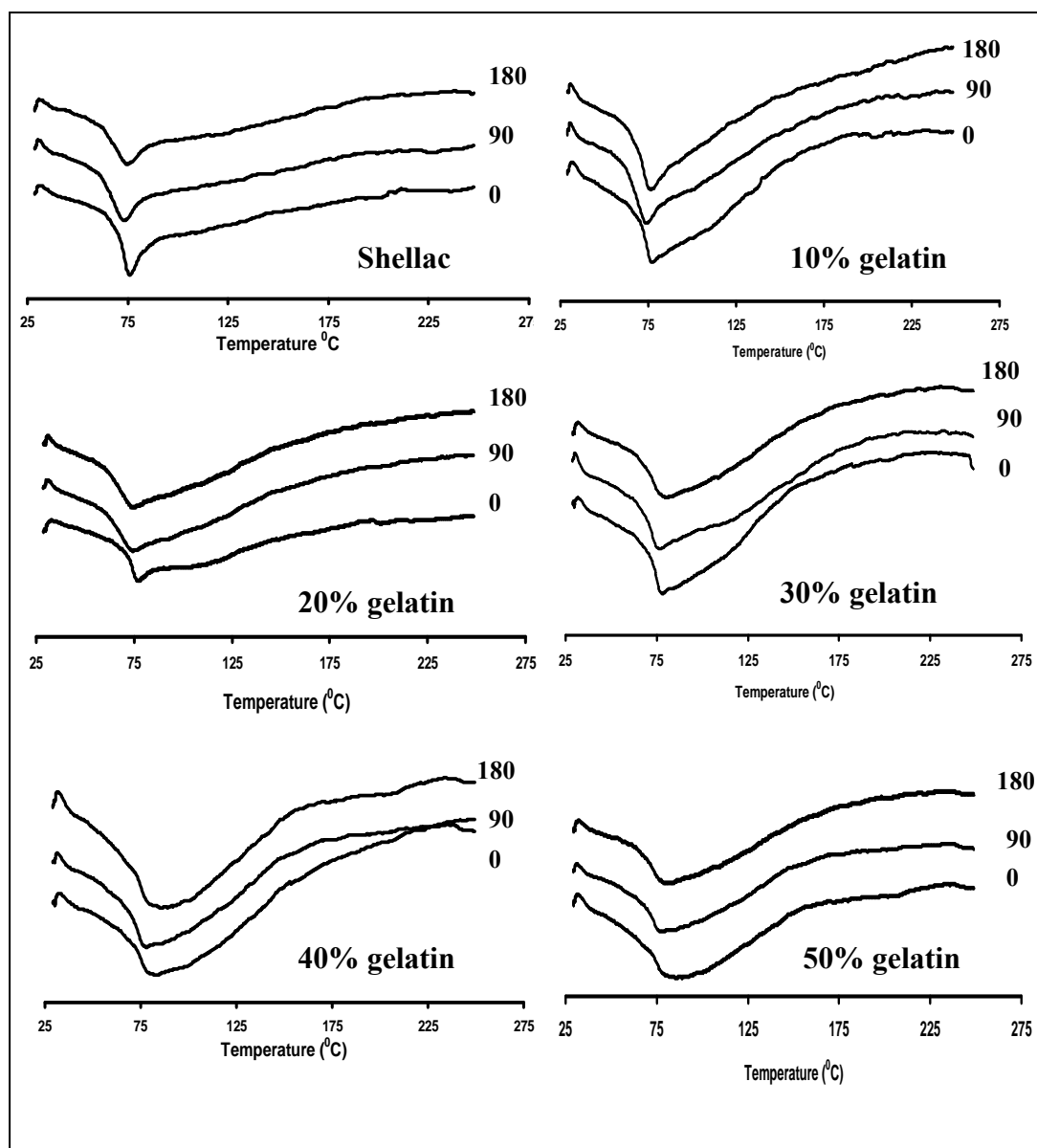


Figure 53 DTA thermogram of composite polymer films varying with the concentrations of gelatin upon storage at 40 °C, 75% RH for 180 days

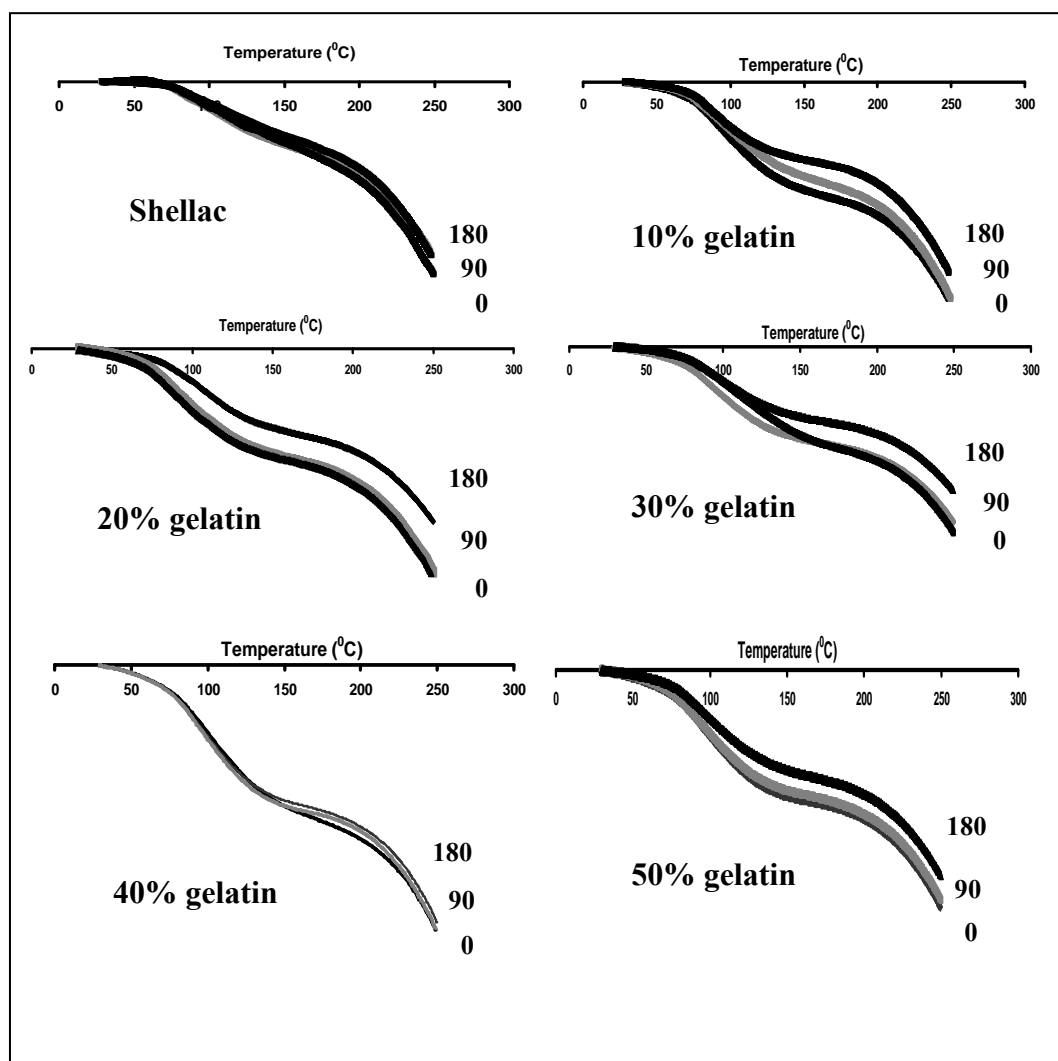


Figure 54 TG thermogram of composite polymer films varying with the concentrations of gelatin upon storage at 40 °C, 75% RH for 180 days

Table 43 Effect of types and concentrations on puncture strength of shellac and gelatin composite polymer film upon storage for 180 days at 40 °C, 75 % RH

Type of polymer film	Puncture strength (MPa)			
	day 0	day 15	day 30	day 60
SHL	3.61 ± 0.90	0.51 ± 0.13	0.54 ± 0.23	0.97 ± 0.35
CF	14.07 ± 3.20	13.25 ± 6.36	17.56 ± 5.07	5.16 ± 2.03
CF + PEG400 5%	11.40 ± 2.24	16.64 ± 2.70	15.91 ± 3.31	13.35 ± 4.31
CF + PEG400 10%	3.71 ± 0.84	5.24 ± 1.51	6.35 ± 2.54	13.83 ± 3.62
CF + DEP5%	12.28 ± 1.80	13.78 ± 2.93	13.48 ± 3.31	13.92 ± 4.71
CF + DEP10%	7.34 ± 0.58	6.69 ± 2.35	15.09 ± 5.17	15.85 ± 4.65

Type of polymer film	Puncture strength (MPa)			
	day 90	day 120	day 150	day 180
SHL	0.68 ± 0.13	0.47 ± 0.10	0.39 ± 0.17	0.29 ± 0.07
CF	1.27 ± 0.87	0.5 ± 0.36	0.54 ± 0.12	0.44 ± 0.22
CF + PEG 400 5%	15.92 ± 2.05	18.4 ± 6.25	19.55 ± 2.21	21.26 ± 5.19
CF + PEG 400 10%	14.33 ± 2.83	17.6 ± 2.60	14.89 ± 3.63	22.12 ± 3.25
CF + DEP 5%	11.39 ± 4.44	11.0 ± 3.61	10.22 ± 1.85	9.27 ± 3.55
CF + DEP 10%	15.57 ± 1.48	13.8 ± 2.21	12.67 ± 4.31	11.36 ± 4.32

Table 44 Effect of types and concentrations on elongation of shellac and gelatin composite polymer film upon storage for 180 days at 40 °C, 75 % RH

Type of polymer film	Elongation (%)			
	day 0	day 15	day 30	day 60
SHL	3.80 ±1.35	1.3 ±0.48	0.60±0.27	1.10±0.73
CF	26.66 ±4.77	23.85±15.41	40.16±8.32	4.62±2.93
CF + PEG 400 5%	63.53 ±13.01	69.91±19.66	46.01±9.16	55.44±12.54
CF + PEG 400 10%	134.28 ±13.49	83.69±19.12	85.69± 26.86	91.25±25.24
CF + DEP 5%	50.69 ±12.18	70.93±14.69	48.79±15.32	41.83±28.94
CF + DEP 10%	108.17± 33.12	80.40±28.02	37.55±12.61	46.39±12.67

Type of polymer film	Elongation (%)			
	day 90	day 120	day 150	day 180
SHL	1.69±0.52	0.51±0.25	1.08±0.58	1.08±0.26
CF	2.72±2.36	2.10±0.70	0.52±0.49	0.52±0.15
CF + PEG 400 5%	44.71±12.09	53.1±14.5	50.77±15.12	42.73±9.94
CF + PEG 400 10%	96.95±28.71	90.3±43.7	84.91±37.05	71.47±15.34
CF + DEP 5%	31.64±12.94	22.2±12.0	40.25±15.84	27.21±10.22
CF + DEP 10%	53.42±10.70	71.3±31.5	43.52±11.11	30.26±15.03

Table 45 Effect of types and concentrations on acid value of shellac and gelatin composite polymer film upon storage for 180 days at 40 °C, 75 % RH

Type of polymer film	AV (mg KOH/g shellac)			
	day 0	day 15	day 30	day 60
SHL	76.00±0.43	74.75±1.34	75.30±0.57	71.88±0.40
CF	62.00±0.18	62.02±1.37	60.53±0.44	62.47±0.88
CF + PEG 400 5%	68.48±1.05	67.67±0.10	66.99±3.54	63.00±0.10
CF + PEG 400 10%	71.81±1.31	69.14±1.20	68.96±2.56	56.32±3.25
CF + DEP 5%	63.98±2.36	61.48±0.50	63.94±4.33	63.11±0.09
CF + DEP 10%	66.58±0.85	64.93±0.52	59.16±0.77	56.42±3.10

Type of polymer film	AV (mg KOH/g shellac)			
	day 90	day 120	day 150	day 180
SHL	72.19±0.57	65.08±0.69	63.72±1.63	58.73±1.65
CF	60.59±0.42	59.63±0.71	60.60±0.67	58.18±2.14
CF + PEG 400 5%	56.04±3.36	57.47±1.10	60.99±1.96	56.69±1.19
CF + PEG 400 10%	58.62±0.37	56.83±1.40	60.40±0.70	59.85±2.87
CF + DEP 5%	62.26±1.41	60.99±2.12	54.06±4.34	52.17±1.41
CF + DEP 10%	52.48±2.12	50.30±0.71	53.41±5.24	46.38±1.04

Table 46 Effect of types and concentrations on insoluble solid of shellac and gelatin composite polymer film upon storage for 180 days at 40 °C, 75 % RH

Type of polymer film	IS (%)			
	day 0	day 15	day 30	day 60
SHL	0.74±0.04	0.93±0.06	1.04±0.29	7.32±0.33
CF	0.27±0.06	0.23±0.14	0.32±0.04	0.66±0.06
CF + PEG 400 5%	0.29±0.10	0.47±0.08	0.45±0.14	0.52±0.36
CF + PEG 400 10%	0.53±0.03	0.45±0.16	1.23±0.09	0.66±0.02
CF + DEP 5%	0.44±0.13	0.75±0.09	0.72±0.06	0.94±0.05
CF + DEP 10%	0.50±0.04	0.50±0.14	0.55±0.19	0.65±0.26

Type of polymer film	IS (%)			
	day 90	day 120	day 150	day 180
SHL	11.18±0.46	23.40±0.39	39.77±2.59	51.69±0.63
CF	0.86±0.17	1.37±0.50	1.31±0.34	1.61±0.08
CF + PEG 400 5%	0.52±0.06	1.64±0.21	1.88±0.45	2.11±0.70
CF + PEG 400 10%	0.91±0.04	1.93±0.01	2.67±0.75	3.60±0.86
CF + DEP 5%	1.15±0.15	3.04±1.01	5.63±1.24	7.24±0.46
CF + DEP 10%	1.06±0.48	3.42±0.43	8.00±1.34	12.89±1.64

Table 47 Effect of types and concentrations of plasticizers on wettability of composite polymer based on shellac and gelatin upon storage at 40 °C, 75% RH for 180 days when water was used at standard liquid

Type of polymer film	Contact angle (degree)		
	day 0	day 90	day 180
SHL	81.39 ± 1.32	83.34 ± 3.30	92.01 ± 1.18
CF	70.89 ± 0.72	75.61 ± 0.89	76.50 ± 1.20
CF + PEG 400 5%	67.55 ± 0.77	69.71 ± 0.50	71.87 ± 1.35
CF + PEG 400 10%	65.74 ± 0.93	67.25 ± 1.22	69.35 ± 0.53
CF + DEP 5%	76.12 ± 1.90	81.12 ± 0.61	85.06 ± 4.66
CF + DEP 10%	79.64 ± 3.61	84.69 ± 1.62	88.17 ± 0.64

Table 48 Effect of types and concentrations of plasticizers on wettability of composite polymer based on shellac and gelatin upon storage at 40 °C, 75% RH for 180 days when formamide was used at standard liquid

Type of polymer film	Contact angle (degree)		
	day 0	day 90	day 180
SHL	57.72 ± 0.68	65.35 ± 5.01	69.35 ± 5.01
CF	48.95 ± 1.08	54.78 ± 2.57	57.56 ± 1.57
CF + PEG 400 5%	44.80 ± 2.01	45.51 ± 1.52	48.82 ± 1.52
CF + PEG 400 10%	40.41 ± 0.36	42.76 ± 2.20	44.57 ± 0.88
CF + DEP 5%	53.37 ± 4.44	56.00 ± 1.67	60.80 ± 1.15
CF + DEP 10%	56.25 ± 1.83	59.52 ± 0.71	62.76 ± 1.37

Table 49 Effect of types and concentrations of plasticizers on wettability of shellac and gelatin composite polymers upon storage at 40 °C, 75% RH for 180 days when diiodomethane was used at standard liquid

Type of polymer film	Contact angle (degree)		
	day 0	day 90	day 180
SHL	62.87 ± 1.96	59.87 ± 2.05	55.54 ± 3.14
CF	71.30 ± 5.28	59.15 ± 2.28	56.24 ± 3.37
CF + PEG 400 5%	72.48 ± 1.65	70.72 ± 0.63	66.90 ± 2.87
CF + PEG 400 10%	74.55 ± 1.43	71.41 ± 0.85	74.44 ± 1.27
CF + DEP 5%	65.34 ± 1.67	62.02 ± 1.19	59.03 ± 0.97
CF + DEP 10%	63.43 ± 1.22	65.13 ± 0.86	62.58 ± 1.19

Table 50 Effect of types and concentrations of plasticizers on WVPC of shellac and gelatin composite polymer film upon storage for 180 days at 40 °C, 75 % RH

Types of polymer film	WVPC x 10 <sup>-8</sup> (gh <sup>-1</sup> m <sup>-1</sup> Pa <sup>-1</sup> )		
	day 0	day 90	day 180
SHL	4.15 ± 1.85	2.49 ± 0.26	1.29 ± 0.41
CF	6.12 ± 0.80	4.35 ± 1.38	2.00 ± 0.32
CF + PEG 400 5%	6.55 ± 1.54	5.43 ± 0.23	4.11 ± 0.68
CF + PEG 400 10%	7.95 ± 2.61	7.43 ± 1.15	5.78 ± 1.19
CF + DEP 5%	4.36 ± 0.64	4.13 ± 1.44	3.79 ± 0.82
CF + DEP 10%	2.86 ± 0.65	2.74 ± 0.61	2.45 ± 0.53

Table 51 Effect of types and concentrations of plasticizers on moisture content of shellac and gelatin composite polymer film upon storage for 180 days at 40 °C, 75 % RH

Type of polymer film	Moisture content (%)		
	day 0	day 90	day 180
SHL	8.61 ± 1.00	7.77 ± 0.36	5.03 ± 1.44
CF	12.46 ± 0.28	9.26 ± 0.29	6.16 ± 1.55
CF + PEG 400 5%	14.27 ± 0.57	13.49 ± 0.66	14.45 ± 0.83
CF + PEG 400 10%	16.78 ± 0.49	15.86 ± 1.09	15.50 ± 1.98
CF + DEP 5%	12.68 ± 0.81	11.51 ± 1.49	9.21 ± 1.10
CF + DEP 10%	14.96 ± 1.85	13.52 ± 2.71	11.39 ± 1.17

Table 52 Effect of gelatin content on contact angle of shellac and gelatin composite polymers solution over various substrates

Content of gelatin (% w/w)	Contact angle (degree)	
	Glass	Teflon
0	38.58 ± 1.08	67.13 ± 1.48
10	32.44 ± 2.39	71.45 ± 1.17
20	30.92 ± 3.42	74.92 ± 4.49
30	27.25 ± 2.30	76.62 ± 1.09
40	24.79 ± 1.17	78.97 ± 0.97
50	21.70 ± 0.95	84.47 ± 4.46
100	14.36 ± 2.06	91.88±2.45

Table 53 Effect of gelatin content on contact angle of shellac and gelatin composite polymers solution over various substrates

Content of gelatin (% w/w)	Contact angle (degree)	
	Banana	Mango
0	41.69 ± 1.24	48.55 ± 1.23
10	48.53 ± 1.37	55.18 ± 1.52
20	53.50 ± 2.17	57.41 ± 1.55
30	57.64 ± 2.26	61.15 ± 1.26
40	58.88 ± 1.14	65.85 ± 3.07
50	64.73 ± 1.40	68.33 ± 1.03
100	78.17 ± 1.16	78.98 ± 2.64

Table 54 Effect of gelatin content on contact angle of shellac and gelatin composite polymers solution over various substrates

Content of gelatin (% w/w)	Contact angle (degree)	
	Theophylline	Aspirin
0	64.72 ± 4.24	68.77 ± 1.69
10	55.58 ± 3.36	66.91 ± 2.61
20	46.75 ± 1.65	65.33 ± 1.30
30	42.69 ± 0.91	64.05 ± 1.19
40	37.26 ± 2.08	60.96 ± 1.27
50	34.60 ± 1.66	58.36 ± 0.39
100	21.92 ± 3.27	42.40 ± 2.41

Table 55 Effect of types and concentrations of plasticizers on contact angle of shellac and gelatin composite polymers solution over various substrates

Types of polymer films	Contact angle (degree)	
	Glass	Teflon
SHL	38.58 ± 1.08	67.13 ± 1.48
CF	24.79 ± 1.17	78.97 ± 0.97
CF + PEG 400 5%	22.37 ± 1.40	84.11 ± 1.25
CF + PEG 400 10%	20.39 ± 2.41	89.73 ± 1.90
CF + DEP 5%	30.32 ± 2.99	74.05 ± 1.95
CF + DEP 10%	34.01 ± 1.01	68.66 ± 1.33

Table 56 Effect of types and concentrations of plasticizers on contact angle of shellac and gelatin composite polymers solution over various substrates

Types of polymer films	Contact angle (degree)	
	Banana	Mango
SHL	41.69 ± 1.24	48.55 ± 1.23
CF	58.88 ± 1.14	65.85 ± 3.07
CF + PEG 400 5%	64.80 ± 2.24	71.89 ± 5.71
CF + PEG 400 10%	71.08 ± 4.21	79.28 ± 0.62
CF + DEP 5%	45.33 ± 0.71	54.58 ± 1.11
CF + DEP 10%	39.26 ± 1.56	44.51 ± 4.19

Table 57 Effect of types and concentrations of plasticizers on contact angle of shellac and gelatin composite polymers solution over various substrates

Types of polymer films	Contact angle (degree)	
	Theophylline	Aspirin
SHL	64.72 ± 4.24	68.77 ± 1.69
CF	37.26 ± 2.08	60.96 ± 1.27
CF + PEG 400 5%	32.99 ± 1.10	56.11 ± 1.77
CF + PEG 400 10%	27.92 ± 3.33	51.06 ± 1.14
CF + DEP 5%	45.37 ± 4.18	64.39 ± 0.61
CF + DEP 10%	54.39 ± 2.21	71.33 ± 2.85

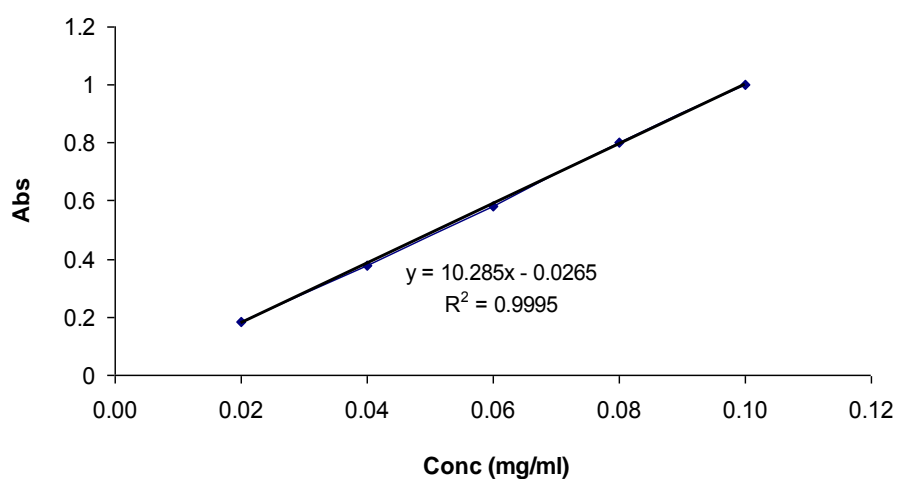


Figure 55 Standard curve of glucose

### Sugar assay (Sample)

$$\begin{aligned}
 \text{Equation from STD} \quad y &= 10.285x - 0.0265 \\
 x &= y/10.285 \\
 &= 0.289 / 10.285 = 0.0281 \\
 \text{Dilute 50 x} &= 0.0281 \times 50 = 1.4050 \text{ mg/ml} \\
 \text{Change from mg/ml to \%} &= (1.4050 \text{ mg/ml} \times 100 \text{ g}) / (1000 \text{ ml} \times 0.2001 \text{ g}) \\
 \% \text{ TSS} &= 0.70 \%
 \end{aligned}$$

Table 58 List of abbreviations

Symbol	Definition
°C	degree Celsius
>	more than
<	less than
%	percent
MPa	miliprasca
mN/m	milinutron per mate
mg	miligram
MW	molecular weight
pK <sub>a</sub>	minus logarithm base 10 of K <sub>a</sub> , -log K <sub>a</sub>
w/w	weight by weight
cm <sup>2</sup>	square centimeter
g	gram
min	minute
h	hours
pH	negative logarithm of the hydrogen ion concentration
WVPC	watet vapor permeability coefficiency
W <sub>a</sub>	work of adhesion
S	spreading coefficient
AV	acid value
IS	insoluble sold
TSS	total soluble sugar
TA	tritible acidity
FTIR	Fourier transformed infrared spectroscopy
PXRD	powder X-ray diffraction
SEM	scanning electron microscope

Table 58 List of abbreviations (continue)

Symbol	Definition
DTA	differential thermal analysis
TG	thermogravimetry
CF	composite polymer film
CF	composite polymer film
SHL	shellac
DEP	diethyl phthalate
PEG 400	polyethylene glycol 400
$\gamma^T_s$	total surface free energy of composite film
$\gamma^P_s$	polar force of solid
$\gamma^D_s$	dispersive force of solid
$\gamma^P_L$	polar forces of liquid surface
$\gamma^D_L$	dispersive forces of liquid surface
$\theta$	degree of contact angle
S0	without coating
S1	shellac coating
S2	shellac–gelatin coating
S3	shellac-gelatin+PEG 400 coating

## BIOGRAPHY

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### Patent

1. Manee Luangtana-anan and Sitthiphong Soradech. “Component and production on stability enhancement of shellac by formation of composite polymer with hydrophilic polymer” **(Submit)**

### Publication

1. Sitthiphong Soradech, Jurairat Nunthanid, Sontaya Limmatvapirat and Manee Luangtana-anan. “Approach for enhancement of mechanical properties and film coating efficiency of shellac by formation of composite film based on shellac and gelatin” **(Submit)**
2. Sitthiphong Soradech, Jurairat Nunthanid, Pornsak Sriamornsak, Sontaya Limmatvapirat and Manee Luangtana-anan. “Factors affecting on an enhancement of mechanical properties of composite film based on shellac and gelatin” **(Submit)**
3. Sitthiphong Soradech, Jurairat Nunthanid, Sontaya Limmatvapirat and Manee Luangtana-anan. “Stability enhancement of shellac by formation of composite polymer with gelatin” **(In preparation)**

**Poster Presentation**

1. Sitthiphong Soradech, Jurairat Nunthanid, Pornsak Sriamornsak, Sontaya Limmatvapirat and Manee Luangtana-anan. “Factors affecting on an enhancement of mechanical properties of composite film based on shellac and gelatin” International Conference on Agriculture and Agro-Industry (ICAAI2010) Food, Health and Trade 19-20 November 2010.
2. Sitthiphong Soradech, Jurairat Nunthanid, Pornsak Sriamornsak, Sontaya Limmatvapirat and Manee Luangtana-anan. “Factors affecting wettability and surface free energy of shellac and gelatin composite film” The 4<sup>th</sup> Annual Research Conference in Silpakorn Research, 19-21 January 2011, Nakornpathom, Thailand, Poster presentation.