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An approach for the enhancement of the mechanical properties and film coating efficiency of shellac by the formation of composite films based on shellac and gelatin

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ABSTRACT

The purpose of this study was to enhance the mechanical properties and film coating efficiency of shellac by the formation of composite films with different concentrations of gelatin. The composite films were prepared by the casting method and their mechanical and physicochemical properties were investigated. The results demonstrated that the puncture strength and percentage elongation of the composite film increased from 3.61 to 15.58 MPa and from 3.80% to 32.47% as the gelatin concentration increased to 50% w/w, respectively, indicating the enhancement of the strength and flexibility of the shellac film. The efficiency of the composite film over two model substrates, i.e., hydrophilic and hydrophobic substrates, respectively, was also studied. The work of adhesion and spreading coefficient of the composite film increased from 66.42 to 83.53 mN/m and from −8.14 to −3.07 mN/m for the hydrophilic substrate, indicating the improvement of the coating efficiency whereas the hydrophobic substrate showed the opposite trend with the increase in gelatin concentration. Therefore, the formation of the composite film not only improved the mechanical properties of shellac but also enhanced the efficiency of film coating by the modification of different concentrations of hydrocolloid polymer to suit with the type of coating substrate. Hence the knowledge of composite film could make beneficial contributions to the various applications in film coating for the food and pharmaceutical industries.

1. Introduction

Shellac, a special natural polymer, obtained from purified resinous secretion of lac insects, *Laccifer Lacca*, has been widely studied as an edible film coating. The insect is mostly cultivated on host trees in India and Thailand (Krause and Müller, 2001; Yu et al., 2006). Shellac is composed of a hard resin and soft resin of polyesters and single esters containing hydroxyl and carboxyl groups (Singh et al., 1974; Upadhye et al., 1970). It is an excellent film forming agent with good barrier properties and soluble in alcohol and alkaline solutions (Limmatvapirat et al., 2004, 2007; Luangtana-anan et al., 2007). The shellac has been widely used in the food and agro industries for water, gas, lipid and microbial spoilage protection and hence prolonging the shelf life of these products (Hagenmaier and Baker, 1993; McGuire and Hagenmaier, 1996; Valencia-Chamorro et al., 2009). It has been used for moisture protection of drugs, controlled drug delivery and enteric coating for drugs in the pharmaceutical industries (Limmatvapirat et al., 2004; Pearnchob et al., 2004). However, edible films made from shellac generally shows poor mechanical strength and brittleness. The puncture strength of native shellac film was 1.0–2.0 MPa and the percentage elongation of native shellac was 1.0–3.0%, lower than those of other natural polymers (Limmatvapirat et al., 2007; Pearnchob et al., 2004). There have been several reports on the improvement of the mechanical properties of shellac by the incorporation of plasticizers, the formation of salt form and the formation of hydrolyzed shellac. However, all these methods could only improve the flexibility; the good strength of shellac was still not reported (Limmatvapirat et al., 2007; Luangtana-anan et al., 2007; Pearnchob et al., 2004).

Composite films are one effective method for improving the drawback of natural polymers by incorporation with a secondary polymer. The composite films made from blending two different polymers can be expected to have better mechanical and barrier properties. Various combinations of two natural polymers are proteins and polysaccharides, proteins and lipids, polysaccharides and lipids or synthetic polymers and natural polymers (Bourtoom, 2008; Yu et al., 2006). The mechanical and barrier properties of composite films strongly depended on the constituting polymer

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characteristics and their compatibility (García et al., 2004). Therefore, the problem of shellac films could be improved by blending with a hydrophilic polymer. The addition of hydrophilic polymers such as hydroxypropyl methylcellulose (HPMC), methylcellulose (MC) and carbomer was generally used to enhance the mechanical and physical properties of shellac films (Qussi and Suess, 2006).

Gelatin, a natural hydrocolloid polymer obtained by hydrolysis of collagen from skin, bones and connective tissue (Gómez-Guillén et al., 2009; Li et al., 2006; Rivero et al., 2009; Martucci and Ruseckaite, 2010; Wang et al., 2009), is a protein widely used in the food, agro, pharmaceutical, and cosmetic industries. It is one of the materials used in edible films and coating, due to its abundance, biodegradability, biocompatibility, low cost, global availability, excellent film forming and good mechanical properties (Vanin et al., 2005; Arvanitoyannis, 1999; Arvanitoyannis et al., 1998a, 1998b, 1997). Many researchers used gelatin as a secondary polymer in blending film preparations (Cao et al., 2007; Cheng et al., 2003; Dong et al., 2006). The maximum values of tensile strength and elongation at breaking were both observed when the content of the gelatin increased (Cao et al., 2007). The blending with gelatin was an effective method for improving the mechanical properties of the drug loaded alginate films (Dong et al., 2006). The flexibility of chitosan films increased when they blended with the higher gelatin concentrations (Cheng et al., 2003). Therefore, gelatin as the hydrophilic polymer was chosen in this study to improve the mechanical property of shellac.

Generally, the coating efficiency of a film can be predicted by the two parameters that are work of adhesion and spreading coefficient which are based on the calculation of the surface free energy (Oh and Luner, 1999). The higher values of work of adhesion and spreading coefficient, the higher the coating efficiency over the substrate surface can be obtained.

Therefore, the objective of the present study was to enhance the mechanical properties and to investigate the film coating efficiency of composite films based on shellac and gelatin. Various concentrations of gelatin were investigated, mixed with shellac in a free film. The composite films were then investigated for their physicochemical properties such as acid value, FTIR spectroscopy, powder X-ray diffraction, mechanical properties, wettability, surface free energy, water content, water solubility, water swelling, moisture sorption isotherm and water vapor permeability coefficient. The composite films were further tested for coating efficiency over hydrophobic and hydrophilic substrates.

2. Material and method

2.1. Materials

Shellac was supplied from Union Shellac Part., Ltd. (Bangkok, Thailand). Gelatin (Type A, 300 blooms) made form porcine skin was purchased from Sigma Aldrich (USA). The solvents used were ammonium solution obtained from Merck (Germany) while formamide and diiodomethane were purchased from Sigma (USA).

2.2. Preparation of composite film based on shellac and gelatin

The shellac and gelatin composite film was prepared by the film casting method. The 6% w/w shellac was dissolved in ammonium solution to prepare shellac in ammonium salt form. The amounts of 28% w/w ammonium salt solutions (NH_3) were calculated on the basis of the acid value of shellac, that is, the amount of salt used to interact with the acid groups of shellac. The shellac solution was then centrifuged for 10 min at 6000 rpm and the insoluble solid was removed by Whatman paper filtration with the aid of a vacuum pump (Limmatvapirat et al., 2007). The 6% w/w gelatin was prepared by hydration at room temperature for 30 min and then dissolved in water at 50 °C with stirring at the rate of 650 rpm for 1 h. The pH of shellac solution was dependent on the ammonia solution excess and was in the range of 8.5–8.75. The 6% w/w composite solutions were prepared by adding different concentrations of gelatin at 10, 20, 30, 40 and 50% w/w into the shellac solution. The composite solutions were homogenized by an ultrasonic generator for 1 min and continuously stirred by a magnetic stirrer for 2 h. All composite solutions were then poured onto a glass plate, the surface of which was treated with silicone solution (Aquasil® Siliconizing Fluids) to help the peeling and were allowed to dry at 50 °C for 6–8 h in a hot air oven. The composite films were kept in a desiccators containing dried silica gel for 1 h to control the moisture of all films prior to testing and evaluation of physicochemical properties. The efficiency of film coating was further tested as predicted by the two parameters, i.e., work of adhesion and spreading coefficient based on the calculation of the surface free energy and contact angle measurement.

2.3. Evaluation of physicochemical properties of composite film based on shellac and gelatin

2.3.1. Films thickness

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

2.3.2. Acid value

The acid value was determined by the acid–base titration method adapted from United Stage Pharmacopeia USP XXIII (USP, 1995). An accurately weighed 2 g of the composite film sample was dissolved in ethanol overnight and finally adjusted to the total weight of 26 g with ethanol. The solution was centrifuged for 10 min at 4000 rpm. Twenty-six grams 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 ml 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 the free carboxyl group of shellac. The amount of shellac was calculated on the ratio of shellac in the composite films. The average of three measurements was performed.

2.3.3. Fourier transformed infrared spectroscopy

The functional group of the film samples 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 carried out for each sample from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}.

2.3.4. Powder X-ray diffraction

The crystallinity and amorphous stage of the film samples were investigated by a Powder X-ray diffractrometer (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^{-1}. All samples were performed in duplicate.

2.3.5. Mechanical properties

The mechanical properties of the films were evaluated by puncture test as described in Limmatvapirat et al. (2008). A texture analyzer (TA.XT. plus Texture Analyzer, Stable Micro Systems, UK)