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Effect of UV-Treatment on Properties of Biodegradable Film From Rice Starch

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***Abstract*—**Photo-crosslinked rice starch-based biodegradable films were prepared by casting film-solution on leveled trays and ultra violet (UV) irradiation was applied for 10 minute. The effect of the content (3%, 6% and 9 wt. %)of photosensitiser (sodium benzoate) on mechanical properties, water vapor permeability (WVP) and structural properties of rice starch films were investigated. The tensile strength increased while elongation at break and water resistance properties of rice starch films decreased with addition and increasing content of photosensitiser. The % crystallinity of rice starch films were decreased when the content of photosensitiser increased and UV were applied. The results showed that the carboxylate group band of sodium benzoate was found in the FTIR spectrum of rice starch films and found that incorporation of 6% of photosensitiser into the films showed a higher absorption band of resulted films. This result pointed out the highest interaction between starch molecules was occurred.

***Keywords*—**Biodegradable film, Rice starch, UV treatment, Photosensitiser, Photo-crosslink

1. Introduction

THE synthesis of polymer for used as a food packaging was research since 50-60 year ago. Synthetics polymers are durable and resistant to biodegrade well [1] but in the present found that polymer residues are significant part of the volume of waste, causing environmental problems because it is not biodegradable and difficult to eliminate and recycle [2]. The increased awareness of environmental conservation and protection has promoted the presentation of biodegradable polymers produced from renewable sources as an alternative to synthetic polymers for selected industrial applications [3].Since 1970s has been studied about polar polymers or biopolymer such as polysaccharide and protein that is the new alternative for used instead of synthetic polymer in plastic and plastic film manufacturing against environmental problems [4]. Previous research found that the property of polysaccharide protein and fat can be form into film and coating. Biopolymer consists of naturally occurring polymers that are found in living organisms. The use of biopolymers will have a less harmful effect on our environment compared to the use of fossil fuel based commodity [5]. Rice is the seed of the monocot plants Oryza sativa or Oryza glaberrima. As a cereal grain, it is the most important staple food for a large part of the world's human population, especially in East and South Asia, the Middle East, Latin America, and the West Indies. It is the grain with the second-highest worldwide production, after maize (corn) [6]. Rice has many important roles in Thai society from food to work. Rice uses over half of the farmable land area and labor force in Thailand. It is one of the main foods and sources of nutrition for most Thai citizens. Chiang Phatthalung rice is native rice that has a high amount of amylose (about 2536. 30.40 %). Because of its high amylose that made it's hard and not favor for Thai consumers. In the other hand, rice starch that has a high amylose which is attractive raw materials for use as barriers in packaging materials. Rice starch have been used to produce biodegradable films to partially or entirely replace plastic polymers because of its low cost and renewability, as well as possessing good mechanical properties [7] However, wide application of starch film is limited by their mechanical weakness and the fact that they are swollen by water the extent of which depends on the relative humidity (RH) [8].

Chemical modifications such as grafting or crosslinking are able to limit excessive water swelling and macromolecular motion. Classical treatments lead to modified starches used in food or paper additive applications in which crosslinking occurs in heterogeneous media using dry or semidry blending process. For example, starch networks are usually performed by treating granular starch with the following crosslinking agents in heterogeneous media: sodium trimetaphosphate [9], epichlorohydrin [10].

Radiation processing technology is being used to improve the properties of polymer product because of its tendency to undergo the chemical reaction between the polymer molecules under irradiation [11]. Reference [12] used photo-additives such as benzoic acid derivatives for poly (vinyl alcohol) crosslinking. The most efficient photo-additive, sodium benzoate, is known to be photolysed by UV irradiation [13], [14] (Fig. 1). Radiation modification of starch-based plastic sheet was studied [15].The investigation showed that the properties of starch based were improved by radiation induced crosslinking. The sensitized irradiated films are rendered insoluble in the solvents in which they were originally soluble [16]. In this study was improved the properties of rice starch film by UV treatment, using sodium benzoate as a photosensitiser. The properties of rice starch film received from UV treatment were compared on mechanical property, thermal property and structural characteristics.

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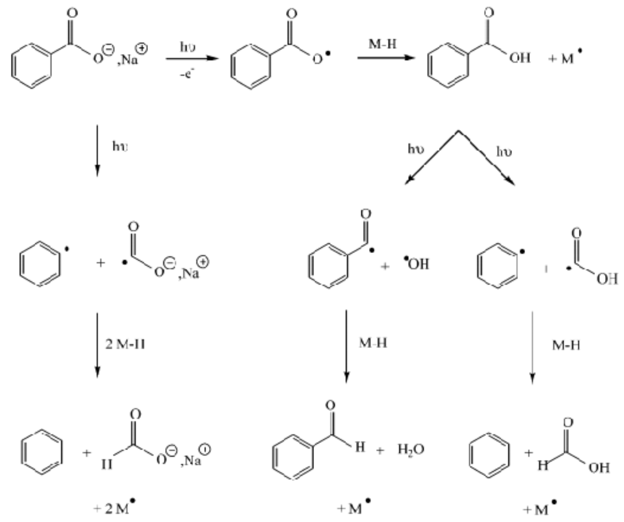

Fig. 1 Mechanism involved in sodium benzoate of irradiated rice starch film [16]

II. Materials And Methods

2.1 Materials

Rice starch was extracted from grains of Chiang Phatthalung rice (Oryza sativa L.) by using alkaline methods, rice grain purchased from a local grocery. Commercial grade sorbitol used as a plasticizer and Sodium benzoate used as photo-sensitizer was purchased from the Vidyasom Co. Ltd. (Thailand).

2.2 Methods

2.2.1 Preparation of UV treated starch film

3% starch solution (w/v) were prepared by adding native rice starch in distilled water with vigorous stirring and heating the slurry to 85ºC (gelatinize temperature) and held at this temperature for 10 min. Then the slurry were cooled to 50±5ºC, sorbitol (plasticizer) was added as 50% of dry wt. starch stirred for 2 min and then sodium benzoate (3%, 6% and 9% w/w of dry wt.) were added as photo-initiator. The mixtures were cast onto flat, leveled, non-stick trays to set. After that the tray were held overnight at 55ºC for 10-12 h. The resulting films were kept in desiccators at 55% RH for 72 h before irradiation as described in following section. All treatments were made in triplicate.

2.2.2 Ultraviolet irradiation set up

Starch films, which were kept at 55% RH, were irradiated under mercury lamp (400W) supplying radiation longer wavelength than 290 nm for 10. After irradiation, UV treated films were kept at 55% RH in a desiccators for 72 h for further testing.

2.2.3 Tensile strength (TS) and elongation at break (E) testing

Tensile strength (TS) was measured with a LLOYD Instrument (Model LR30K, LLOYD Instruments Ltd., Hampshire, England) as per the ASTM D882-91 Standard method [17]. Ten samples, 1.5 cm x 12 cm, were cut from each film. The initial grip separation and cross-head speed were set at 70 mm and 30 mm/min, respectively. Tensile strength was calculated by dividing the maximum force by the initial specimen cross-sectional area, and the present elongation at break (E) was calculated as in (1).

$$E = 100 \times (d_{after} - d_{before}) / d_{before} \quad (1)$$

Where, d was the distance between grips holding the specimen before and after the breaking of the specimen.

2.2.4 Water vapor permeability (WVP)

The gravimetric Modified Cup Method based on the ASTM E96-92 standard method [18] was used to determine the WVP of the films. The test cups were filled with 20 g of silica gel (desiccant) to produce a 0% RH below the film. A sample was placed in between the cup and the ring cover of each cup coated with a silicone sealant (high vacuum grease, Lithelin, Hanau, Germany) and held with four screws around the cup’s circumference. The air gap was approximately 1.5 cm between the film surface and desiccant. The rated water vapor transmissions (WVTR) of each film were measured at 60±2% RH and 25±2°C.

After taking the initial weight of the test cup, it was placed in a growth chamber with an air velocity rate of 135 m/min (Model KBF115, Contherm Scient, Lower Hutt, New Zealand). Weight gain measurements were taken by weighing the test cup to the nearest 0.0001 g with an electronic scale (Satorious Corp.) every 3 h for 18 h. A plot of weight gained versus time was used to determine the WVTR. The slope of the linear portion of this plot represented the steady state amount of water vapor diffusing through the film per unit time (g/h). The WVTR was expressed in gram units, per square meter, per day. Steady state over time (slope) yielded a regression coefficient of 0.99 or greater. Six samples per treatment were tested. The WVP of the film was calculated by multiplying the steady WVTR by the film thickness and dividing that by the water vapor pressure difference across the film.

2.2.5 X-ray diffraction (XRD)

The X-ray patterns of starch powders, starch nanocrystals, starch film, and starch film reinforced with starch nanocrystals were analyzed. This was done by using an X-ray diffractometer (Philips X, Pert MPD, Japan) with Cu Kα radiation at a voltage of 40 kV and 30 mA. The samples were scanned between 2θ = 3-40° with a scanning speed of 2°/min. Prior to testing the samples were dried and stored in desiccators.

2.2.6 Spectroscopic analysis

FT-IR spectra of UV treated rice Starch films were recorded on Bruker Model Equinox 55)Bruker Co., Ettlingen, Germany(The FT-IR samples were mixed with KBr and pressing. The spectra were obtained at a resolution of 4 cm^{-1} in the range 4000 to 400 cm^{-1}.

2.2.7 Statistical analysis

A completely randomized experimental design was used to determine the character of the composite films. Analysis of variance (ANOVA) was used to compare mean differences of the samples. If differences in the means existed, multiple comparisons were performed using Duncan's Multiple Range Test (DMRT).

III. Results And Discussion

3.1 Water vapor permeability (WVP)

As starch is sensitive to moisture, which affects the mechanical properties of thermoplastics starch materials, any improvement in decreasing moisture sensitivity and enhancing water resistance of thermoplastic starch material is seriously important[19]. Water vapor permeability (WVP) results can be useful to understand possible mass transfer mechanism and solute and polymer interactions in biodegradable films. According to the thermodynamic of irreversible process, water chemical potential difference is the driving force of water transfer though a films. When the process occurs at constant temperature and pressure, the water chemical potential difference results proportional to water vapor concentration difference between the two faces [20],[21]. WVP values of untreated and UV treated films are given in Fig. 2. The photo-crosslinked films showed better water barrier properties than untreated films. The resulted demonstrated that WVP values decreased when the amount of sodium benzoate increased. However, the WVP value was slowly increased when the amount of sensitizer was excessive. Since the over amount of photochemical filter which limits UV penetration into the exposed film, so leading to a lower cross-linking density, characterized by cross-linking gradient [22],[16]. The results showed that the WVP of untreated film was 6.19 g.mm/m^2.day.KPa, whereas UV treated rice starch films incorporated with 6% sodium benzoate had the lowest WVP at about 4.12 g.mm/m^2.day.KPa. According to these results could be explained by a hydrophilic group (OH^-) of rice starch decreased when crosslinking reaction occurred between rice starch and sodium benzoate molecules and 6% of sodium benzoate UV treated film has a highest cross-linking density.

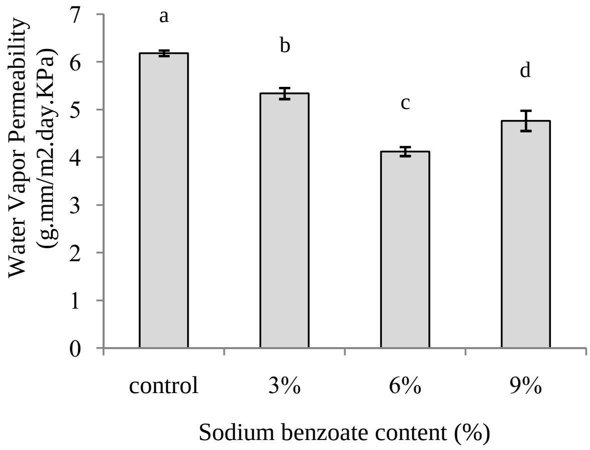

Fig. 2 Effect of content of sodium benzoate on water vapor permeability (WVP) of untreated and UV treated rice starch films. Mean values with different letter are significantly different ($p<0.05$)

3.2. Tensile strength (TS) and Elongation at break (E)

The effect content of photosensitiser on tensile strength (TS) and elongation at break (E) of rice starch films presented in Fig. 3 (a) and (b). Tensile strength is the maximum tensile stress sustained by the sample during the tension test. If maximum tensile stress occurs at either the yield point or the breaking point, it is designated tensile at yield or at break, respectively [23]. The TS of rice starch films increased when incorporation and content of sodium benzoate increased and maximum TS was observed when 6% sodium benzoate was used (Fig. 3(A)). Increasing of TS is due to the increase of crosslinking density. The crosslinking reaction occurs through a radical mechanism, the photosensitiser (sodium benzoate) are excited or decompose to produce radicals upon irradiation with UV light and this radical reacted with starch molecule as cross-linking reaction to increase the tensile strength of UV treated rice starch films, however too much photosensitiser could inhibited UV penetrated and decreased hydrogen abstraction [16]. In generally, food packaging requires high stress with deformation according to the intended application to protect the stuff while in used [24]. According to the results demonstrated that the amount of photosensitiser yielded a good mechanical properties of rice starch films were in the rang of 0.1-6% by used sorbital as plasticizer. Elongation at break (E) is an indication of the films flexibility and stretchability (extensibility), which is determined at point when the film breaks under tensile testing and is expressed as the percentage of change of the original length of the specimen. Fig. 3(B) showed the effect of UV treatment and content of sodium benzoate on E rice starch films, it indicated that E value was decrease from 116% to 67% when amount of photosensitiser increase from 3-6 wt% and E value were slowly increased when photosensitiser increased (9 wt%).

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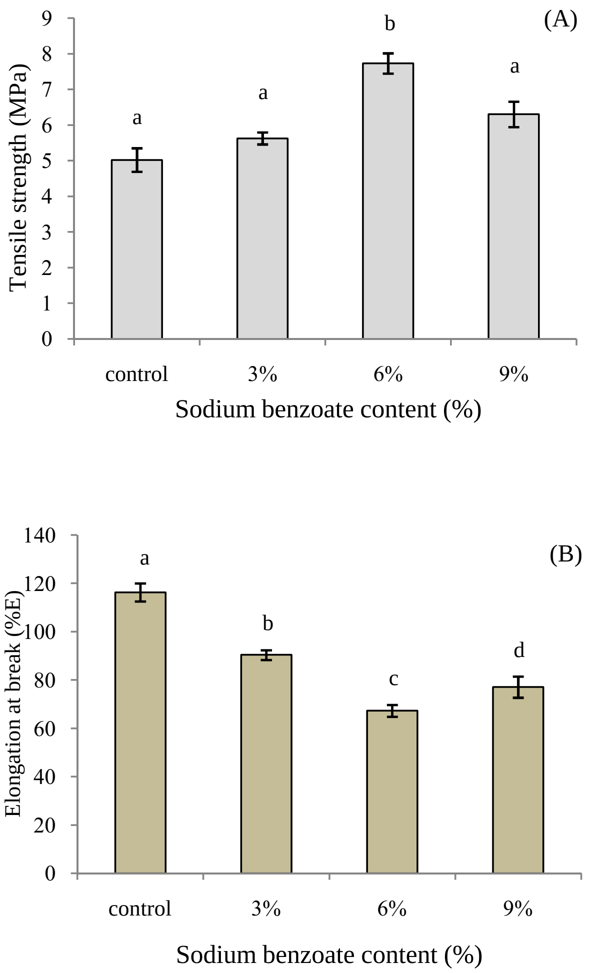


Fig. 3 Effect of content of sodium benzoate on tensile strength (A) and elongation at break (B) of UV treated rice starch films. Mean values with different letter are significantly different ($p<0.05$)

3.3 XRD analysis

The XRD graphs of the individual components; rice starch powder, rice starch film and UV treated rich starch film contained photosensitiser, showed in Fig. 4. It well known that rice starch has the A-type XRD pattern [25] with strong reflection at 16.8, 18.0 and 22.7º and the % crystallinity values were estimated as 23.19%. The characteristic diffraction peaks of rice starch film at 17.5º and 20.5º and UV treated rice starch films were observed at 20.5º. The gelatinized rice starch films had difference structure. The amorphous structure was observed in rice starch film [26]. The crystallinity values of rice starch film (untreated), 3% photosensitiser, 6% photosensitiser and 9% photosensitiser were estimated as 16.10%, 15.95%, 14.97% and 14.79%, respectively. The reduction of % crystallinity is due to starch was gelatinized for forming film, after gelatinization the crystalline of starch granules were destroyed [27] and their participation in cross-linking reaction [28]. The results suggested that the crosslinking reaction decreased the crystallinity of rice starch films because the increase in density fluctuation as an increase of lattice defects introduced by crosslinks within the crystalline phase or to the change in local density in the vicinity of the crosslinks in the amorphous phase[29]. Hence, UV treatment of starch has been reported not to alter the crystalline structure of starch or its gelatinization enthalpy [30].

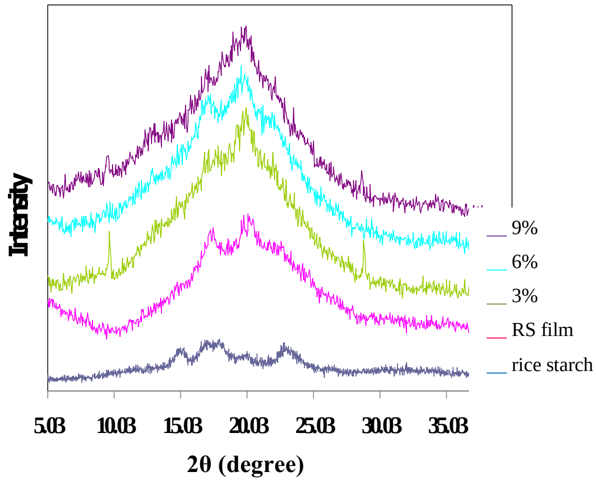
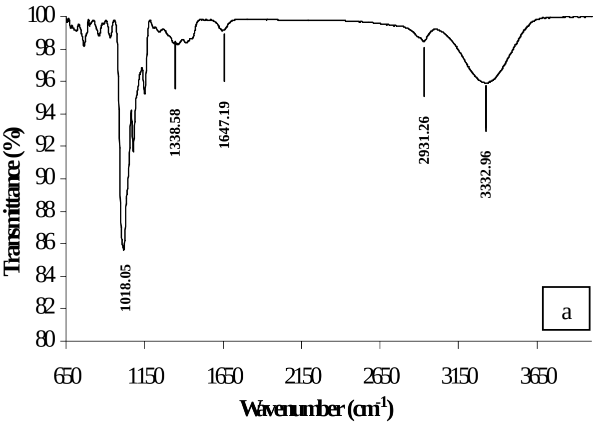
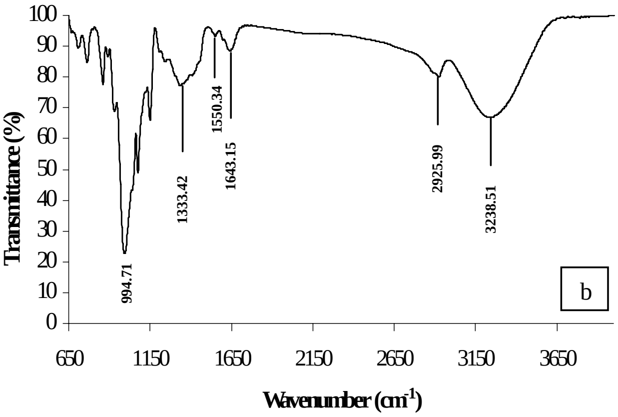


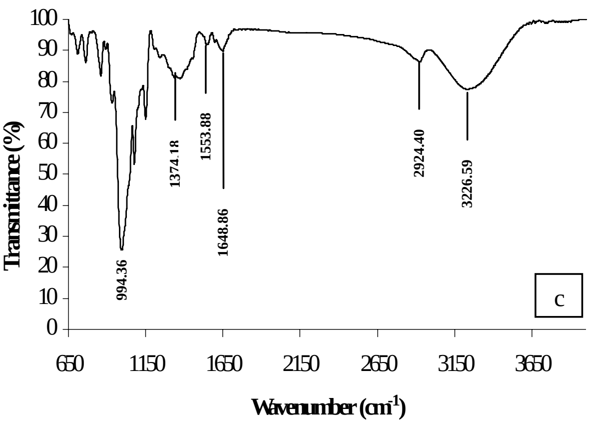
Fig. 4 XRD pattern of rice starch powder, rice starch films (control) and UV treated rice starch films (3%, 6% and 9% of photosensitiser)

3.4 FT-IR analysis

FTIR spectra of all films are presented in Fig. 5(a)-(d). In Fig. 4a are the broad band of rice starch film at 3332.96 cm^{-1} was the O-H stretching. The peak at 2931.26 cm^{-1} corresponded to the C-H stretching, while the band at 1338.58 cm^{-1} was the O-H of water. The UV treated rice starch films spectrum (Fig. 4b-d) demonstrated a weak intensity peak that should corresponding to the benzoate anion and benzoic acid. The peak at 1550.34, 1553.88 and 1550.02 cm^{-1} (3%. 6% and 9% photosensitiser, respectively) corresponded to the CO_2^- asymmetric (ν_{as}) and the peak at 1374.18 and 1380.73 cm^{-1} (6% and 9% photosensitiser) corresponded to the CO_2^- symmetric (ν_s) stretching vibrations of carboxylate group [31]. Additionally, the 6% photosensitiser showed the highest absorption peak at 1553.88 cm^{-1} confirmed 6% photosensitiser film had a higher decomposed of free radicals of sodium benzoate than 3% and 9% photosensitiser. As UV light provides lower energy level than other source of ionizing radiation, it is impossible for direct cleavage of C-C or C-H bond of starch molecules to occur for the formation of free radical. Hence, for crosslinking propose, there need for photosensitiser (photo innitiator) that can absorb a low-energy photon (UV light) and become activated, leading to the formation of free radicals [32] and also leads to macroradical combination by hydrogen abstraction [16]. Which films that had a high free radical, it could occurred a high crosslinking reaction between rice starch molecules.







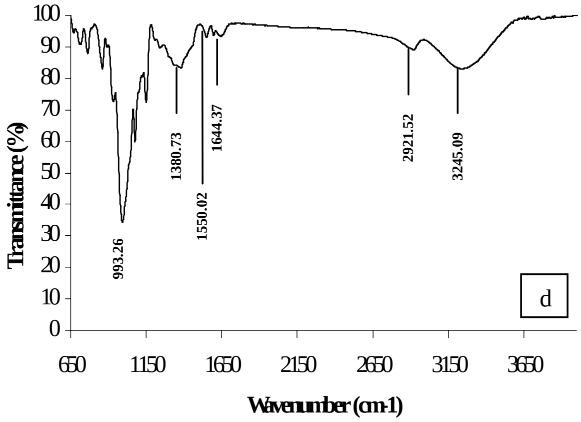


Fig. 4 Attenuated total reflection (ATR) spectra of rice starch film (a) and UV treated rice starch films; 3% (b), 6% (c) and 9% (d) of photosensitiser

IV. Conclusions

Rice starch films prepared by solution casting on leveled trays using sorbitol as plasticizer and sodium benzoate as photosensitiser were successfully crosslinked by UV treatment. The reaction was confirmed by FTIR and X-ray diffraction analyses of UV treated rice starch films indicated that the free radicals of photosensitiser were created from UV irradiation and 6% photosensitiser has highest crosslink density. Increasing amount of photosensitiser decreased the %crystallinity of rice starch film due to crosslinking reaction and inhibiting crystalline. The WVP of rice starch film was found to decrease after UV treatment. Improvement of mechanical properties of rice starch film was successful when the content of photosensitiser increased, however excessive content of photosensitiser content (9%) inhibited crosllinking reactivity resulted in decreasing in mechanical of rice starch films.

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