Effect of UV-treatment on the properties of biodegradable rice starch films

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Abstract

Rice starch biodegradable films were prepared by casting film solution on leveled trays and ultra violet (UV) irradiation for 10 min was applied. The influence of content (3%, 6% and 9 wt. %) of the photosensitizer (sodium benzoate) on the properties of rice starch films was investigated. The tensile strength and gel fraction increased but elongation at break, water barrier properties, degree of swelling and crystalline peak structure of rice starch films decreased with additional and increasing content of the photosensitizer. However, too high a level of photosensitizer (9%) yielded lowering properties in the resulting films, but it was still much higher than untreated rice starch films. It was observed that incorporation of photosensitizer into the rice starch films increased lightness and made it yellowish but decreased transparency. The results showed that the carboxylate group band of sodium benzoate in the FTIR spectrum was present in the rice starch films. These results pointed out that there was an interaction between starch molecules induced by the photosensitizer. In addition, the highest absorption band resulted from cross linking reaction activity was observed when 6% photosensitizer was applied.

Introduction

Renewable resources are again of importance in our modern society because of their positive effects on agriculture, the environment and the economy (Kaplan, 1998). The synthesis of polymer for used as food packaging has been researched since 50-60 year ago. Synthetics polymers are durable and resistant to biodegrading as well (Mali *et al*., 2002) but it has presently been found that polymer residues are a significant part of the volume of waste, causing environmental problems because it is not biodegradable and difficult to eliminate and recycle (Carvalho *et al*., 2007). 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 (Muñoz *et al*., 2003). Since the 1970s polar polymers or biopolymer such as polysaccharide and protein have been studied as new alternatives for use instead of synthetic polymer in plastic and plastic film manufacturing to take account of environmental problems (Garcia *et al*., 2000). Previous research found that a property of polysaccharide protein and fat is that it can be formed 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 plastics (Krochta and De Mulder-Johnston, 1997).

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 that is the second-highest in worldwide production, after maize (corn) (Cohen *et al*., 1994). 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 25.36-30.40%). Because of its high amylose it is hard and not favored by Thai consumers. On the other hand, rice starch that has a high amylose is attractive as raw materials for use as barriers in packaging materials. Rice starch has 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 (Xu *et al*., 2005) However, the wide application of starch film is limited by their mechanical weaknesses and the fact that they are swollen by water depending on the relative humidity (RH) (Seow *et al*., 1999).

Ultraviolet (UV) irradiation as a physical, cost

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effective, non-thermal, and environmental-friendly technology has received increasing attention during recent years. During this time it has been successfully applied for the preservation and decontamination of food products (Bintsis *et al.*, 2000). UV irradiation has been used in medical and pharmaceutical research to crosslink collagen and gelatin films (Bhat and Karim, 2009). Using UV irradiation requires the presence in the biological medium of certain substances known as photosensitizers which induce changes in the biological substrate after absorbing appropriate radiation (Spielmann *et al.*, 1994). The most efficient photosensitizers, such as sodium benzoate, are known to be photolysed by UV irradiation (Ghosp and Gangopadhay, 2000). The sensitized irradiated films are rendered insoluble in the solvents in which they were originally soluble (Deville *et al.*, 2002). The aim of this study was to improve the properties of rice starch film by UV treatment and sodium benzoate was used as the photosensitizer. The properties of rice starch film received from UV treatment such as physico-mechanical properties, thermal properties and structural characteristics were considered.

Materials and Methods

Materials

Rice starch was extracted from grains of Chiang Phatthalung rice (*Oryza sativa* L.) by using alkaline methods. The rice grain was purchased from a local grocery. It had amylose and moisture content of about 30.40% and 12.19% (determined in triplicate by vacuum drying at 70°C and <1 mmHg pressure for 24 h using the EYELA™, Model VOS-300VD, Japan). Commercial grade sorbitol was purchased from the Vidyasom Co. Ltd. (Thailand).

Film preparation

A starch solution with a concentration of 3% (w/v) was prepared by dispersing rice starch in distilled water and heating the mixtures and stirring until it gelatinized (85°C for 5 min). It was then cooled to 45±2°C. Sorbitol was added as 40% of the starch. The mixtures were cast onto flat, leveled, non-stick trays to set. Once set, the trays were held overnight at 55°C for 10 h undisturbed, and then cooled to an ambient temperature before peeling the films off the plates. The film samples were stored in plastic bags and held in desiccators at 50±5% RH for further testing. All treatments were made in triplicate.

Ultraviolet irradiation set up

Starch films, which were kept at 50±5% RH, were irradiated under mercury lamp (400W) supplying radiation longer wavelength than 290 nm for 10, 20 and 30 min. After irradiation, UV treated films were kept at 55% RH in a desiccators for 72 h for further testing.

Film testing

Conditioning

All films were conditioned prior to subjecting them to permeability and mechanical tests according to a standard method, D618-61 (ASTM, 1993). Films used for testing water vapor permeability (WVP), tensile strength (TS), and elongation (E) were conditioned at 55±5% RH and 27±2°C by placing them in desiccators over a saturated solution of $Mg(NO_3)_2.6H_2O$ for 72 hours or more. For other tests, film samples were transferred to plastic bags after peeling and placed in desiccators.

Film thickness

The thickness of the films was measured with a precision digital micrometer (Digimatic Indicator, Mitutoyo Corporation, Japan) to the nearest 0.0001 (±5%) at five random locations on the film. The mean thickness values for each sample were calculated and used in water vapor permeability (WVP) and tensile strength (TS) calculations.

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

Tensile strength (TS) was measured with a LLOYD Instrument (Model LR30K, LLOYD Instruments Ltd., Hampshire, England) using the ASTM D882-91 Standard method (ASTM, 1993). Ten samples, 1.5 cm x 12 cm, were cut from each film. The initial grip separation and crosshead 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).

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

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

Water vapor permeability (WVP)

The gravimetric Modified Cup Method based on the ASTM E96-92 standard method (McHugh *et al.*, 1993) 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 of 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 water vapor permeability 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.

Color and transparency

Color of the films was determined using a CIE colorimeter (Hunter associates laboratory, Inc., Reston, Virginia, USA), working with D65 (day light). The color parameters were expressed as L^* (lightness), a^* (redness/greenness) and b^* (yellowness/blueness) values. The transparency value of film was calculated by the following equation (Han and Floros, 1997):

$$\text{Transparency value} = -\log T600/x$$

where T600 is the fractional transmittance at 600 nm and x is the film thickness (mm). The greater value represents the lower transparency of the film.

X-ray diffraction

The X-ray patterns of starch powders, starch nanocrystals, starch film, and starch film reinforced with starch nanocrystals were analyzed 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 $2\theta = 3\text{-}40°$ with a scanning speed of 2°/min. Prior to testing the samples were dried and stored in desiccators.

Spectroscopic analysis

FT-IR spectra of UV treated rice Starch films were recorded on a 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}.

Swelling degree and gel fraction measurement

Photo-crosslinking was characterized by swelling behavior in dimethylsulphoxide (DMSO) in which neat starch is completely soluble. The method was described by Delville et al. (2002). Starch films were irradiated in conditions at 55% RH for 72 h before immersion in DMSO at 25ºC for 24 h (sorption equilibrium). The swollen film was weighted (ms) and washed with water and ethanol respectively in order to remove the DMSO. Thereafter swollen film was dried at 80ºC for 24 h and reconditioned at 55% RH before weighing (md). The swelling Degree (SD) was calculated as in (1).

$$\text{Swelling Degree (SD)} = \frac{m_s - m_d}{m_d} \approx \frac{m_s}{m_d} \; ; m_d \ll m_s \quad (1)$$

The gel fraction (GF) was calculated as in (2).

$$\text{Gel fraction (GF)} \; 100 \frac{m_d}{m_c} \quad (2)$$

Where mc is a corrected weight (that is only starch weight content).

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).

Results and Discussion

Tensile strength and Elongation at break

Rice starch films may be subjected to various kinds of stress during use; the determination of the mechanical properties involves not only scientific but also technological and practical aspects. Tensile strength (TS) 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 strength at yield or at break respectively (ASTM, 1995). Elongation at break is an indication of a film's flexibility and stretchability (extensibility). This is determined as the point when the film breaks under tensile testing. It is expressed as the percentage of change of the original length of the specimen between the grips of a film to the extent of the stretch (Gontard et al., 1992).

The effect of the content of photosensitizer on tensile strength and elongation at break of rice starch films is depicted in Figure 1 (A) and (B). The tensile strength of rice starch film was affected by the content of photosensitizer. The results demonstrate that the

tensile strength of rice starch films was enhanced with the addition of photosensitizer. Furthermore, increasing the photosensitizer content from 3 to 6% resulted in an increase in tensile strength. However, the tensile strength showed a decrease when 9% photosensitizer was used (Figure 1(A)). Increasing the tensile strength was due to the high interaction that occurs between starch molecules and the performances (such as mechanical properties) and the increase of crosslinking density. The crosslinking reaction occurs through a radical mechanism. Technically, the photosensitizer (sodium benzoate) is excited or decomposed to produce radicals upon irradiation with UV light and this radical reacted with starch molecule as a cross-linking reaction that increased the tensile strength of UV treated rice starch films. However too much photosensitizer (9%) could inhibit UV penetrated and decreases the hydrogen abstraction (Delville *et al.*, 2002). The results pointed out that when the photosensitizer acted the tensile strength value was decreased. The results are similar to the study of Follain *et al.* (2005) who studied the impact of the addition of poly vinyl alcohol and photo cross-linking on starch based materials' mechanical properties.

The mechanical properties of starch/PVA blends, with or without cross-linking, have been analyzed in order to study how the increase in the linear to branched chain can improve the material's performances. As a result, the mechanical properties of the films obtained were enhanced when photo cross-linking was applied. In addition, Khan *et al.* (2006) also prepared and characterized ultra violet (UV) radiation cured bio-degradable films from sago starch and a polyvinyl alcohol blend. They found that UV irradiation could promote the degree of cross-linking of sago starch and polyvinyl alcohol blend film. The tensile strength values of the resulting films increased with UV radiation doses up to a certain limit and then decreased. According to these results the crosslinking reaction between starch and polyvinyl alcohol molecules may induce while UV light penetrated into starch/PVA film. However, too much photosensitizer would inhibit UV penetration and decrease hydrogen abstraction (Delville *et al.*, 2002). Its mean outcome when the photosensitizer accessed the tensile strength was decreased.

Moreover, Kumar and Singh (2008) showed the improvement in the properties of starch biocomposites films brought about by photo-induced crosslinking. In this study, the starch biocomposites films were prepared from the aqueous dispersions of starch with microcrystalline cellulose using glycerol as plasticizer and irradiated under ultraviolet (UV) light

using sodium benzoate as photosensitizer. The results showed that, the tensile modulus and strength were found to improve when photo-irradiation was applied. It is assumed that treating starch biocomposites films with photo cross-linking under ultraviolet could improve their physical and mechanical properties. These results demonstrate that the amount of photosensitizer provided to rice starch films resulting in good mechanical properties were in the range 3-6% when using sorbitol as a plasticizer. Figure 1(B) shows the effect of photosensitizer content on elongation at break on UV treated rice starch films. It was found that the elongation at break of rice starch films decreased from 116% to 67% when the amount of photosensitizer increased from 3-6 wt%. The elongation at break slowly increased when 9% photosensitizer was added. This phenomenon indicated the critical content of the greatest interaction of the rice starch polymer chain. The experiments showed that tensile strength and elongation at break of rice starch films are almost inversely related.
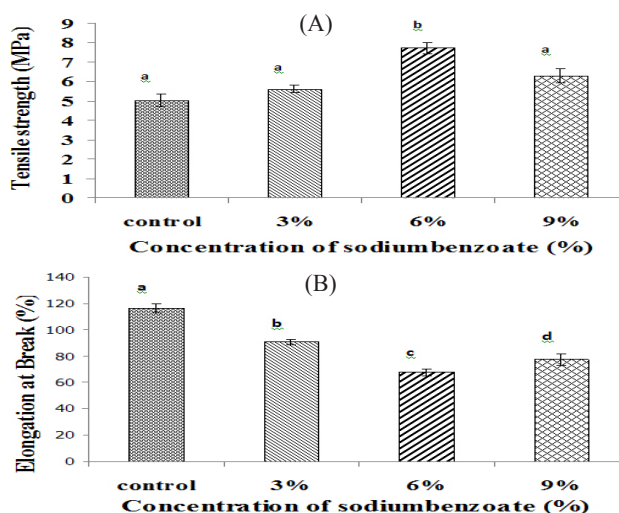

Figure 1. Effect of content of sodium benzoate (photosensitizer) on tensile strength (A) and elongation at break (B) of UV treated rice starch films. Mean values with different letter are significantly different (p < 0.05).

Water vapor permeability

Biodegradable films produced from polysaccharides, however, are highly sensitive to water and provide limited resistance to moisture transmission. This is due to the substantial inherent hydrophilicity of the film-forming substances and to the considerable amount of hydrophilic plasticizers incorporated into the films (Guilbert, 1986; Krochta, 1992; Gennadios *et al.*, 1994; Guilbert *et al.*, 1996; Callegarin *et al.*, 1997). Permeability is influenced by the hydrophobic or hydrophilic nature of the material, by the presence of voids or cracks, and by the stearic hindrance and tortuosity in the structure (Wang *et al.*, 2005; Ghanbarzadeh *et al.*, 2006).

Water vapor permeability results can be useful to understand possible mass transfer mechanisms and solute and polymer interactions in biodegradable films. According to the thermodynamic of irreversible process, the water chemical potential difference is the driving force of water transfer though a film. When the process occurs at constant temperatures and pressure, the water chemical potential difference results are proportional to the water vapor concentration difference between the two faces (Morillon *et al.*, 2000; Bertuzzi *et al.*, 2007). Water vapor permeability values of untreated rice starch films and UV treated rice starch films are shown in Figure 2. The UV treated rice starch films showed lower water vapor permeability than untreated rice starch films. The results show that water vapor permeability decreased when the amount of photosensitizer increased. However, the water vapor permeability value was slowly increased when the amount of photosensitizer was excessive. This is because the amount of photosensitizer filter limits UV penetration into the exposed film, hence leading to a lower crosslinking density, characterized by the crosslinking gradient (Decker and Moussa, 1990; Delville *et al.*, 2002). The water vapor permeability of untreated rice starch film was 6.19 g.mm/m^2.day.KPa, whereas the UV treated rice starch films containing photosensitizer had water vapor permeability between 5.34 to 4.12 g.mm/m^2.day.KPa. The results showed that the lowest water vapor permeability was observed when 6% photosensitizer was applied (4.12 g.mm/m^2.day.KPa.).
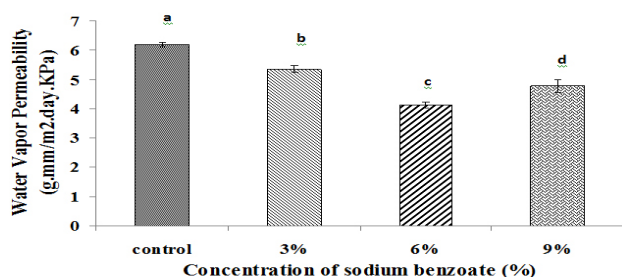

Figure 2. Effect of content of sodium benzoate (photosensitizer) on water vapor permeability of UV treated rice starch films. Mean values with different letter are significantly different (p < 0.05).

These results could be explained by a hydrophilic group (OH-) of rice starch decreasing when a crosslinking reaction occurred between rice starch and photosensitizer molecules;thus using 6% photosensitizer provided the highest crosslinking density. Sabato *et al.* (2001) reported that crosslinked soy and whey protein based films with gamma-irradiation showed decreased water vapor permeability in the presence of carboxymethylcellulose (CMC). Crosslinking has been shown to increase resistance

to water vapor and transporting gas (Ghanbarzadeh *et al.*, 2006).

Color and transparency

The color of the packaging is an important factor in terms of general appearance and consumer acceptance (Srinivasa *et al.*, 2007). The results of the measurements performed on the rice starch film's color were expressed in accordance with the CIELAB system and the rectangular coordinates (L*, a* and b*). Figure 3 (A-C) shows the effect of photosensitizer on the color of rice starch films. The results demonstrated that photosensitizer content had little effect on the color of rice starch film. However, it was found that a* value tended to decrease when the amount of photosensitizer increased, whereas the L* and b* value increased. It was observed that the addition of photosensitizer into the rice starch film yielded increases in both lightness and yellowness due to the oxidation reaction that induced was by UV light (Hamaguchp *et al.*, 2003). However, too much photosensitizer (9%) provided a decrease of b* value because the excessive amount of photosensitizer limited UV penetration into the films (Delville *et al.*, 2002).
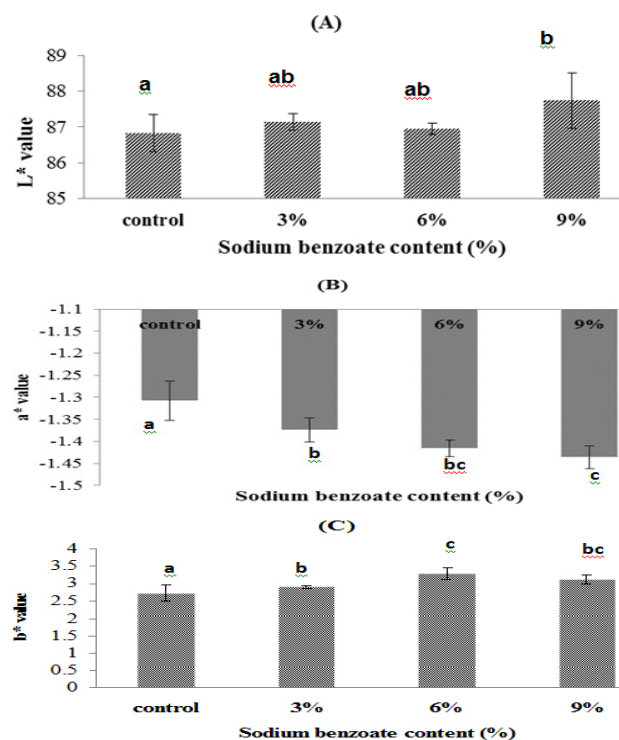

Figure 3. Effect of content of sodium benzoate (photosensitizer) on L* (A); a* (B) and b* (C) of rice starch film and UV treated rice starch films. Mean values with different letters are significantly different (p < 0.05).

Figure 4 shows the transparency value of rice starch films and UV treated rice starch films containing various amounts of photosensitizer. Usually the transparency may be affected by various factors
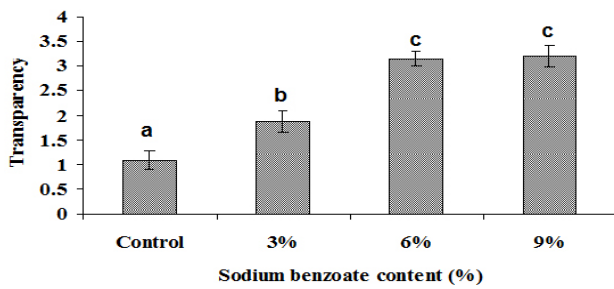
Figure 4. Effect of content of sodium benzoate (photosensitizer) on transparency of rice starch film and UV treated rice starch films. Mean values with different letters are significantly different (p < 0.05).

Table 1. Relative crystallinity of rice starch powder, rice starch film and UV treated rice starch films with various amounts of photosensitizer

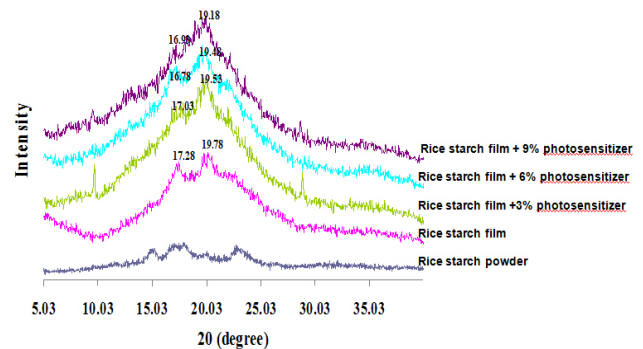| Treatments	%Crystallinity = (A(peak)/A(total)x100)
Rice starch powder	23.19
Rice starch film	16.10
Rice starch film +3% photosensitizer	15.95
Rice starch film +6% photosensitizer	14.97
Rice starch film +6% photosensitizer	14.79

Figure 5. XRD patterns of rice starch powder, rice starch film and UV treated rice starch films contained various amounts of photosensitizer.

including the thickness of the film (Bangyekan *et al.*, 2006). This is also of importance in some instances, such as when used as packaging materials (Phattaraporn *et al.*, 2010). The results showed that the addition of photosensitizer resulted in decreasing transparency. The transparency value of rice starch film was 1.09 and those of UV treated rice starch film were 1.87 - 3.2. Rice starch film without UV treatment showed the highest transparency (the lowest transparency value). The decrease in transparency could possibly arise from the higher interaction between starch molecules when the photosensitizer was applied. The scattering resulted from the retarding of light transmission to the rice starch films. At high photosensitizer content, the rice starch films demonstrated lower transparency than with less photosensitizer. It could be said that presence of photosensitizer and exposing the films to UV light decreased the transparency of the resulting films.

X-ray Diffraction analysis

The XRD graphs of the individual components, rice starch powder, rice starch film and UV treated rich starch film, containing various amounts of photosensitizer is presented in Figure 5. Technically, different types of crystallinity have been revealed by X-ray diffraction depending on the amylose content of the starch (Van Soest *et al.*, 1996a,b), the origin of the starch (Forssell *et al.*, 1999), the transformation process used (thermo molding, extrusion or casting) (Van Soest *et al.*, 1996a,b; Miles *et al.*, 1985; Rindlav-Westing *et al.*, 1998), and the additives used. It is well known that rice starch has the A-type XRD pattern (Bao and Bergman, 2004) with strong reflection at 15.29º, 17.29º and 22.73º due to the high amylopectin content (Liu *et al.*, 2009) and the % values of the crystallinity were estimated as 23.19% (Table 1).

The characteristic diffraction peaks of rice starch film were present at 17.5º and 20.5º and in the UV treated rice starch films these were observed at about 16º and 20.5º. The gelatinized rice starch films and

UV treated rice starch films had difference structures due to the presence of plasticizer and the crosslink reaction in rice starch molecule. Ummi-Shafiqah *et al.* (2012) reported that the XRD pattern of sago and mung bean starch blend films and UV treated starch blend films could be assigned to a B-type. Starch films normally show a B-type x-ray diffraction, regardless of the original polymorphs of starch from which the films were made (Bader and Göritz, 1994; Rindlav *et al.*, 1997; Rindlav-Westling *et al.*, 1998; Mali *et al.*, 2002; Myllärinen *et al.*, 2002). The results show that the percentage of crystallinity values of untreated rice starch film and rice starch film containing 3%, 6% and 9% photosensitizer were estimated as 16.10%, 15.95%, 14.97% and 14.79%, respectively (Table 1). The reduction of the % crystallinity of rice starch films was because starch was gelatinized in forming the film; after gelatinization the crystallinity of the starch granules was destroyed (Yu *et al.*, 2007) as was their participation in the cross-linking reaction (Das *et al.*, 2010). The results suggested that the crosslinking reaction decreased the crystallinity of rice starch films. This was because of the increase in density fluctuation was an increase in the lattice defects introduced by crosslinking within the crystalline phase, or to the change in local density in the vicinity of the crosslinking in the amorphous phase (Chen and Yeh, 1991). Hence, the UV treatment of starch did not alter the crystalline structure of the starch or its gelatinization enthalpy (Mestres and Rouau, 1997).

Differential scanning calorimeter (DSC)

DSC was used to examine the transition temperatures, such as glass transition temperature (T_g) and specific heat change values (ΔCp), of the films. The crosslinking effect of UV treatment is reflected in the starch being resistant to high temperature, low pH, and high shear, and with improved viscosity and textural properties compared with untreated starch. The photosensitizer binds neighboring anhydroglucose units (AGU) in the amorphous regions of the rice starch amylopectin. In this experiment, the DSC measurements were performed for untreated rice starch films (the control) and UV treated rice starch films. All the samples were heated from -50 to 180°C with a heating rate of 20°C/min. The DSC scan showed wide endothermic peaks around 25°C to 140°C and no exothermic peak was observed during heating (data not shown). The transition temperature obtained from the DSC curve is shown in Table 2.

Table 2. Glass transition temperatures and specific heat change values of rice starch film and UV treated rice starch films containing various amounts of photosensitizer

Treatments	Transition temperature (ºC)			Cp
	T_g onset	T_g midpoint	T_g endpoint	(J/g* ºC)
Rice starch film	23.33	25.60	27.00	0.001195
Rice starch film + 3% photosensitizer	23.67	27.67	28.67	0.003673
Rice starch film + 6% photosensitizer	24	29.37	32.42	0.070471
Rice starch film + 9% photosensitizer	23.45	30.33	33.67	0.06852

The results show the T_g of rice starch film was 25.60ºC and that of the UV treated rice starch films contained 3%, 6% and 9% of photosensitizer was 27.67ºC, 29.37ºC and 30.33ºC, respectively. In addition, the results show that the enthalpy (DH) of the films was enhanced with the addition of photosensitizer. This was inferred through taking into account the concomitant increase in the interaction of the starch molecules. Furthermore, increasing the photosensitizer content from 3 to 6% resulted in an increase of enthalpy (Table 2). Technically, the T_g is a very important physical parameter, which serves to explain the physical and chemical behavior of material systems, and is defined as the temperature at which the material changes from the glassy state to the rubbery state for a given heating rate (Perdomo *et al.*, 2009). This transition was associated with the molecular segmental motion of the amorphous structure. These results reveal that treated rice starch film showed a slight increase in T_g due to the crosslinking between the polymer chain that occurred which resulted in decreased chain mobility in the amorphous region of the resulting film matrix. The results are similar to the study by Bhat and Karim (2009) who investigated commercially procured fish gelatin treated with UV light to improve the properties of fish gelatin. They reported that enthalpy (DH) showed a significant increase after UV treatment. This increase might be attributed to the UV-induced crosslinking of fish gelatin.

FT-IR analysis

The FTIR spectra of all films are presented in Figure 6. The broad band of rice starch film at 3332.96 cm⁻¹ was due to 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 demonstrated a weak intensity peak that should correspond to benzoate anion and benzoic acid. The peak at 1550.34, 1553.88 and 1550.02 cm⁻¹ (3%. 6% and 9% photosensitizer, respectively) corresponded to the CO_2- asymmetric (v_{as}) and the peak at 1374.18 and 1380.73 cm⁻¹ (6% and 9% photosensitizer) corresponded to the CO_2- symmetric (v_s) stretching vibrations of the carboxylate group (Tejedor *et al.*, 1992). In addition, the 6% photosensitizer showed the highest absorption peak at 1553.88 cm⁻¹. This confirmed that the 6% photosensitizer film had a higher level of decomposed free radicals of sodium benzoate than the 3% and 9% photosensitizer film.

As UV light provides a 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 radicals. Hence, for crosslinking purposes, there is need for a photosensitizer (photo initiator) that can absorb a low-energy photon (UV light) and become activated. This leads to the formation of free radicals (Bhat and Karim, 2009) and also leads to macro radical combination by hydrogen abstraction (Delville *et al.*, 2002). The films that had high free radicals could provide a high crosslinking of rice starch molecules.

Swelling degree and gel fraction

The degree of crosslinking of the starch macromolecular network formed by crosslinking due to UV irradiation can be characterized by the swelling degree and gel fraction (Table 3). Gel fraction is directly related to the mass of starch macromolecules involved in the crosslink network and the swelling degree is related to the density of the newly created network (Zhou *et al.*, 2008). The results show that the gel fraction decrease was concomitant with the increase of swelling degree when the photosensitizer content increased. The swelling degree decreased and

gel fraction increased with the addition and increasing of photosensitizer, which is characteristic of network formation (Delville *et al.*, 2002). The results show that rice starch films containing 6% photosensitizer yielded the lowest of swelling degree and the highest gel fraction. It could be said that the highest crosslinking reaction between starch molecules occurred when 6% photosensitizer was used. However, an inverse trend was observed when 9% was applied. This was because using too much photosensitizer could inhibit UV penetration and decreased hydrogen abstraction resulted in decreasing in molecular interactions. Delville *et al*. (2002) also showed that a network structure formation occurred during the UV irradiation of wheat starch films using sodium benzoate as a photosensitizer. They reported that crosslinking densities can be varied by altering the amount of photosensitizer.

Table 3. Swelling degree and gel fraction of rice starch film and UV treated rice starch films contained various amounts of photosensitizer

Treatments	Swelling degree	Gel fraction
Rice starch film	6.53+0.45	83.99+0.66
Rice starch film + 3% photosensitizer	4.86+0.05	85.61+1.80
Rice starch film + 6% photosensitizer	3.62+0.07	86.77+1.67
Rice starch film + 9% photosensitizer	4.39+0.16	84.49+2.27

Conclusions

Rice starch films prepared by solution casting on leveled trays using sorbitol as plasticizer and sodium benzoate as the photosensitizer were successfully crosslinked by UV treatment. The free radicals of the photosensitizer were created from UV irradiation, confirmed by FTIR, X-ray diffraction analyses including swelling degree and gel fractions values. The highest crosslink density of starch molecules occurred when 6% photosensitizer was used. An improvement in the mechanical and water barrier properties of rice starch film was achieved when the level of the photosensitizer increased. However an excessively high photosensitizer content (9%) inhibited crosslinking reactivity and resulted in a decrease in the mechanical and water barrier properties of the resulting rice starch films.

Acknowledgments

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