Mechanical, thermal and structural properties of rice starch films reinforced with rice starch nanocrystals

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Abstract

A rice starch based film, reinforced with starch nanocrystals (prepared by submitting native granules of rice starch to acid hydrolysis at 40 ºC) was prepared by casting film-solution on leveled trays. The influence of the content of starch nanocrystals (5 to 30%) on the mechanical, thermal and structural properties of rice starch films was investigated. The rice starch films showed an increase in tensile strength but decreasing elongation at break and water barrier properties with the addition of rice starch nanocrystals. The addition of starch nanocrystals increased the crystalline peak structure of rice starch film. However, too high starch nanocrystals content resulted in a decreased crystallinity of the resulting film. The behavior of the thermal properties of rice starch films reinforced with starch nanocrystals was investigated by means of dynamic mechanical thermal analysis, differential scanning calorimeter and thermogravimetric analysis. No endothermic peaks were observed in the glass transition temperature (T_g) of the rice starch film. However, increasing endothermic heat flow was observed when addition and increasing of starch nanocrystals in rice starch films. This can restrict the mobility of the starch chain due to the establishment of strong interactions between rice starch and starch nanocrystals. In addition, a lower content of starch nanocrystals showed smoother than high starch nanocrystals in a rice starch film matrix,

Introduction

In recent years, the environmental pollution from consumed polymers has become serious, particularly from packaging materials and off-set plastic bags and cups. The growing interest in the environmental impact of discarded plastics has led to research on the development of plastics that degrade more rapidly in the environment, leading to a complete mineralization or bio-assimilation of plastics (Aminabhavi *et al*., 1990). 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). Starch is one of the most studied and promising raw materials for the production of biodegradable plastics; it is a natural renewable carbohydrate polymer obtained from a great variety of crops. Starch is a low-cost material compared to most synthetic plastics, and it is readily available. Starch has been investigated widely for the potential manufacture of products such as water-soluble pouches for detergents and insecticides, flushable liners and bags, and medical delivery systems and devices (Fishman *et al*., 2000). Starch consists primarily of branched and linear chains of glucose molecules, namely amylopectin and amylose, respectively. Amylose is essentially a linear molecule with a few branches, whereas amylopectin is a highly branched molecule. A preponderance of amylose in starches gives stronger films. The branched structure of amylopectin generally leads to films with different mechanical properties, such as decreased tensile stress (Tharanathan, 2003).

Rice is the most widely consumed basic food in the world. Each year over 500 million tons of rice is harvested, providing sustenance to many countries and people throughout the world. The unique properties of rice starches are found in its many varieties. Due to different climates, soil characteristics and cultures, over 240,000 registered varieties of rice exist in the world. These varieties lead to a wide range of rice starches with many different characteristics including

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different starting gelatinization temperatures, textures, processing stabilities and viscosities. They have been used to produce biodegradable films to partially or entirely replace plastic polymers because of their 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 its mechanical properties and the efficient barriers against low polarity compounds (Kester and Fennema, 1986). This constraint has led to the development of the improved properties of rice-based films by modifying its starch properties and/or incorporating other materials. Jagannath *et al*. (2003) blended starch with different proteins to decrease the water vapor permeability of the films and to increase their tensile strength. However, starch-based materials have some drawbacks, including poor mechanical properties, high moisture sensitivity and the releasing of small molecular plasticizer from the starch matrix (Zhang *et al*., 2007). Polysaccharides such as cellulose, starch and chitin are potential renewable sources of nanosized reinforcement. They are naturally found in a semicrystalline state and aqueous acids can be employed to hydrolyze the amorphous section of the polymer. Consequentially, the crystalline sections found in these naturally occurring polysaccharides are released, resulting in individual monocrystalline nanoparticles. The particles obtained display different shapes depending on the polysaccharide source; these are rigid rod-like particles for cellulose and platelets for starch (Azizi *et al*., 2005). The preparation and morphological characterization of platelet-like nanoparticles by acid hydrolysis of starch granules has been reported (Putaux *et al*., 2003). They consist of crystalline nanoplatelets about 6-8 nm thick with a length of 20-40 nm and a width of 15-30 nm. The main advantages of such fillers are: their renewable nature; availability; high specific strength; non-abrasive nature that allows easier processing even at high filling levels; biodegradability; and a relatively reactive surface which can be modified accordingly (Angles *et al*., 1999). Thus nanocomposites obtained by the incorporation of nanofillers in both synthetic polymeric matrixes (Chazeau *et al*., 1999) and biopolymers (Angles and Dufresne, 2000) showed desirable improvement of different properties. These were related, for example, with mechanical reinforcement and/or water resistance. A rice starch film has been developed in previous work (Boortoom and Chinnan, 2008). It has been observed that the functional properties of rice starch film, such as its ductility and effectiveness as a barrier, are generally poor. Hence, the objective of this present work was to produce rice starch based nanocomposites

using starch nanocrystals. The effects of the starch nanocrystals on the properties of rice starch films were assessed in terms of their mechanical, thermal and structural characteristics.

Materials

Native rice starch prepared by alkaline methods from rice grains (Chiang Phatthalung) were purchased from a local grocery in Phatthalung province. 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 EYELATM, Model VOS-300VD, Japan). Commercial grade sorbitol was purchased from the Vidyasom Co. Ltd. (Thailand).

Methods

Preparation of starch nanocrystals

Rice starch nanocrystals dispersion was prepared by a previously described method by Angellier *et al*. (2004) with minor modifications. Native rice starch granules weighing 36 g were mixed with 3 M of sulfuric acid (H_2SO_4) solution in a 500 mL Erlenmeyer flask. The suspensions were then continuously stirred at 100 rpm at 40°C. After 5 days of hydrolysis, the suspensions were washed by successive centrifugations in distilled water until neutrality was achieved. This suspension was freeze-dried using freeze dryer. The resulting nanocrystals are generally observed in the form of aggregates having an average size of around 3.97 µm, as measured by Laser particle size analyzer (Model LS-230, Coulter, U.S.A.).

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. Subsequently, the starch nanocrystals dispersion was added at 5, 10, 15, 20, 25, and 30% of starch and stirred for 2 min. 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 60% RH for further testing. All treatments were made in triplicate.

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 $Mg(NO_3)_2 \cdot 6H_2O$ 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).

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

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 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.

Differential scanning calorimeter (DSC)

The thermal properties of rice starch films were analyzed with a Perkin-Elmer DSC-7 (Norwalk, Conn., U.S.A.) equipped with an intra-coolant Thermal Analysis Controller TAC7/DX (Perkin-Elmer). Samples (approx. 20 mg each, db) were weighed into stainless steel pans (Perkin-Elmer) designed to withstand high pressures. The stainless steel pan was sealed with an O-ring, and allowed to reach equilibrium of the moisture overnight. An empty DSC pan was used as a reference pan. The heating rate was programmed by holding the heat at -50°C for 1 min, followed by ramping the temperature range of -50°C to 180°C at a rate of 20 °C/min, and holding it at 180°C for 1 min. The measurements were made at least in duplicate for each treatment.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis was performed to study the degradation characteristics of the films. The thermal stability of each sample was determined using a Perkin-Elmer, TGA7 with a heating rate of 10°C/min in a nitrogen environment. It had a weighting capacity of 0.1 g. Samples were heated from room temperature to 500°C.

Dynamic mechanical thermal analysis (DMTA)

The small deformation analysis of the films was performed in tension mode in a dynamic mechanical thermal analyzer (Rheometric Scientific, DMTA V). The tested filmstrips were cut into small strips (20 x 5 mm) and champed in the instrument with an initial grip separation of 5.5 mm. The films were subjected to a sinusoidal strain on top of static deformation. The testing was conducted at a constant frequency of 1 Hz and a strain of 0.02% over a temperature range

of 50 to 200°C, at a heating rate of 5°C/min. The measurements at each experimental point were done at least in triplicate. Dynamic mechanical spectroscopy was employed within the linear viscoelastic regime to determine T_g. The storage and loss modulus (E' and E'') and loss tangent (tan $\delta = \Delta E'/E''$) were measured as a function of temperature at a constant frequency and a selected heating or cooling rate.

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 2θ = 3-40° with a scanning speed of 2°/min. Prior to testing the samples were dried and stored in desiccators.

Morphology

The morphology of the rice starch films was observed with a Scanning Electron Microscope (SEM, JSM-5800 LV, JEOL, Tokyo, Japan). The size of the rice starch and starch nanocrystals was observed using a Laser particle size analyzer (LS-230, Coulter, U.S.A.).

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 (TS) and elongation at break (ε)

Food packaging generally requires high stress with deformation in accordance with the intended application. In general, food packaging must be an undeformable material to provide structural integrity or to reinforce food structure, or a deformable film for other applications (Gontard et al., 1992). 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 the TS at yield or at break, respectively (ASTM, 1995). The dependence of the TS on the starch nanocrystals content of the rice starch films is shown in Figure 1A. The TS of the control films (unfilled starch nanocrystals) was 7.12 MPa. When the starch nanocrystals was added to rice starch
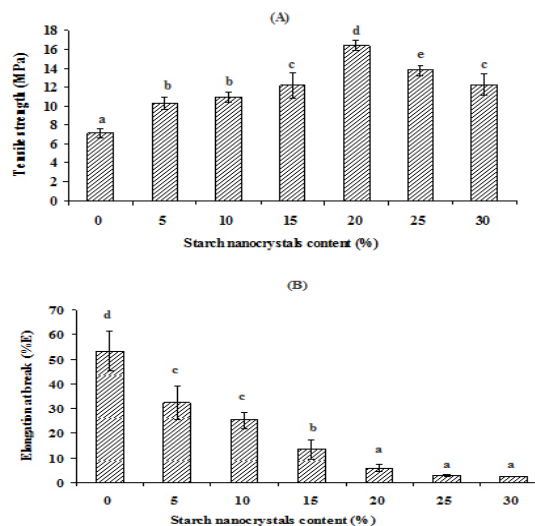

Figure 1. Effect of starch nanocrystals content on tensile strength (A) and elongation at break (B) of rice starch films. Mean values with different letter are significantly different (p<0.05)

films, the TS of the resulting films increased with the starch nanocrystals content. It reached a maximum point at about 20 wt% of the starch nanocrystals, thus achieving a TS of 16.43 MPa. However, when the starch nanocrystals content exceeded 20%, the TS of rice starch films tended to decrease (Figure 1A), but it was still much higher than that of the control film. Owing to the very high specific surface area provided by nanoparticles, the filler-matrix interfacial interactions play a key role in the mechanical properties of nanocomposites (Wetzel et al., 2003). Well distributed particles with an adequate interfacial bonding between filler and matrix allow the effective transfer of stress through a shear mechanism from the matrix to the particles. This can carry the load efficiently and enhance the strength of the composite (Wetzel et al., 2003; Sihna and Okamoto, 2003; Brown and Ellyin, 2005; Abdelmouleh et al., 2005). Similarly, Kristo and Biliaderis (2007) reported significant increases in the TS with increases in the starch nanofiller content. This illustrated the great reinforcing effect of starch nanocrystals addition on plasticized pullulan films. Such a reinforcing effect was also observed in thermoplastic starch filled with waxy maize starch nanocrystals (Angellier et al., 2005) and in cellulose fiber reinforced thermoplastic starch or silk fibroin (Averous et al., 2001; Noshiki et al., 2002).

Elongation at break (ε) is an indication of the film's flexibility and stretch-ability (extensibility). This is determined at the point when the film breaks under tensile testing and is expressed as the percentage of stretching or extending from the original length of the film. The dependence of ε on the starch nanocrystals content of the nanocomposite

films is shown in Figure 1B. The ε of the rice starch films decreased from 53.46% to a minimum of 2.48% when the starch nanocrystals content increased from 5 to 30%. The experiments showed that the TS and ε of nanocomposite films are almost inversely related. This is because the increased brittleness of the composite material induces a decrease in ε. The decrease in ε with the rigid filler addition is a well known phenomenon that is related to the differences in the rigidity between the matrix and fillers. Because of the rigid nature of the fillers, most of the system deformation under high strain comes from the polymer. Consequently, the actual deformation experienced by the polymeric matrix only is much greater than the measured deformation of the sample (Angles *et al*., 1999; Wetzel *et al*., 2003). Similar results were observed by Angellier *et al*. (2006) reported that the unfilled matrix is a viscoelastic material, characterized by a low TS and high ε. As expected, the addition of nanocrystals allows the TS to be increased significantly but also leads to a drastic decrease of the ε. They compare the reinforcing effect of starch nanocrystals to those of tunicin whiskers, because of the organic nature of both fillers and the similar nature of the matrix material used. Chen *et al*. (2008) indicated that the addition of pea starch granules could improve the mechanical properties of the composite. This further proves that starch nanocrystals with smaller size disperses more homogeneously and forms stronger interactions with the matrix than native starch granules. Furthermore, Liu *et al*. (2010) reported that when the bamboo cellulosic crystals content was increased the TS of starch composite films increased sharply. This was because when the size of particle was greatly reduced, many interesting phenomena occurred as a result of the larger surface area and higher surface energy. However, the ε increased when the bamboo cellulosic crystals decreased.

Water vapor permeability (WVP)

Water vapor permeability is proportionally constant and assumed to be independent of the water vapor pressure gradient applied across the films. However, hydrophilic materials such as protein films deviate from this ideal behavior due to the interactions of permeating water molecules with polar groups in the film structure (Haggenmaier and Shaw, 1990). Deviation from the ideal behavior can also be induced by the effects of the structure on materials (Myers *et al*., 1962). A main function of food packaging is often to avoid or least to decrease moisture transfer between the food and the surrounding atmosphere, or between two components of a heterogeneous food
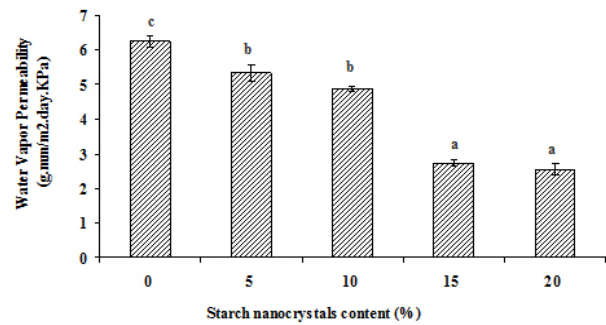

Figure 2. Effect of starch nanocrystals content on water vapor permeability of rice starch films. Mean values with different letter are significantly different (p<0.05)

product. Thus the water vapor permeability should be as low as possible (Gontard *et al*., 1992). Water vapor permeability determination of rice starch films containing 25 % and 30% could not be performed since films were broken during the assays due to their brittleness. Hence, only 5% to 20% starch nanocrystals were dealt with in this study. The effect of starch nanocrystals content on the WVP of rice starch films is shown in Figure 2. It can be seen that WVP of rice starch films decreased significantly with the addition of starch nanocrystals and decreased slowly with an increase in starch nanocrystals content. This was because the water resistance of starch nanocrystals was better than rice starch matrix and the starch nanocrystals dispersed well in the matrix of starch. This provided fewer paths for the water molecules to pass through the composites (Chang *et al*., 2010). The WVP of the control films (unfilled starch nanocrystals) was 6.25 g.mm/m².day. KPa, whereas rice starch film containing starch 20% nanocrystals had the lowest WVP at about 2.56 g.mm/m².day.KPa. The presence of such high filler concentrations probably introduced a tortuous path for water molecules to pass through. The longer diffusive path that the penetrant molecules must travel leads to the reduction of permeability (Sihna and Okamoto, 2003). The starch nanoparticles most likely to form a continuous pathway for the diffusion of water molecules through the composite are those where the filler content does not exceed 20% (w/w) at high loading levels. The starch nanocrystals probably forms a compact network structure, making the pathway of the permeate complex and decreasing its diffusion through the composite system (Beall, 200). A similar trend was observed in the composites prepare by Kristo and Biliaderis (2007). In addition, Mathew and Dufrene (2002) indicated that the WVP of starch/polyvinyl alcohol blend films decrease with an increase in nano-SiO₂ content. This might indicate the existence of intermolecular interactions and a decrease in the mobility of both the starch and PVA
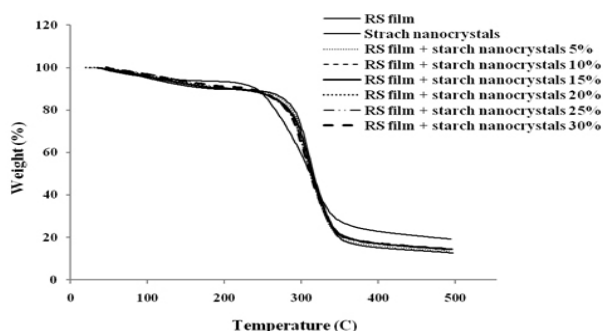
Figure 3. Figure 3 TGA thermograms of starch nanocrystals, rice starch films reinforced with starch nanocrystals at 5-30%

when the nano-SiO$_2$ was added to the solution. In addition, the WVP of potato starch film reinforced by chitin nanoparticle was decreased by increasing the chitin nanoparticles concentration (Chang *et al.*, 2010)

Thermogravimetric Analysis (TGA)

TGA thermograms and char yields of starch nanocrystals, rice starch film and rice starch films reinforced with starch nanocrystals (in the temperature range 50 to 500°C under nitrogen) are shown in Figure 3. The initial weight loss of all samples at approximately 60°C is due to the evaporation of water. The weight loss in the second range (250-300°C) corresponds to a complex process including the dehydration of the saccharide rings and depolymerization (Mathew and Dufrene, 2002). According to the results, the char yield of starch nanocrystals at about 19.23% and the behavior of T$_g$ curves were similar in the composites films (Figure 3). The TGA curves showed that all rice starch film reinforced with starch nanocrystals are stable up to 250°C with a maximum rate of decomposition occurring at about 340°C. The results showed that, the char yield of rice starch film was less (12.7%) than rice starch films reinforced with starch nanocrystals (13.4-14.5%). This was due to the greater thermal stability of the starch nanocrystals. With regard to this result, the mainly composition of the starch nanocrystals are crystals that had strong structures. Therefore, the addition of starch nanocrystals into rice starch film can improve the thermal stability of rice starch films. It was found that the char yield of rice starch film was enhanced as starch nanocrystals filler content increased from 0 to 30% of the starch. These results indicated that addition of starch nanocrystals increased the thermal stability of rice starch films. This is in agreement with the results reported by Wang *et al*. (2010) for composites with starch nanocrystals and incorporating starch nanocrystals and cellulose whiskers in a waterborn polyeurethane

(WPU) matrix. The films containing polysaccharide nanocrystals, especially the ternary system, exhibited higher thermal resistance than pure WPU. It is worth noting that the addition of nanofillers displayed a more distinct effect on improving the thermal resistance of the hard segment. However the rate of the thermal decomposition of the soft segment was even faster than that of pure WPU. This could be explained by the strong hydrogen bonding interactions that existed between the nanofillers and the hard segments, especially in the ternary system. These interactions induced the microphase separation between the hard and soft segments. This led to the acceleration of the decomposition of the soft segments. However, the incorporation of starch nanocrystals and cellulose whiskers also exhibited a much better reinforcing effect than starch nanocrystals reinforced in WPU. This was because jammed hydrogen bonding networks of polysaccharide nanocrystals and whiskers formed in the nanocomposite films. This caused the synergistic reinforcement of the WPU networks. Similarly, Kaushik *et al*. (2010) found that increasing the cellulose nanofibril content led to increased in the char yield of composites films. This is due to cellulose-based composites having lower water content at equilibrium, compared to unfilled thermoplastic starch. As cellulose is crystalline, its crystallinity decreased the polar character of starch. Thus the addition of cellulose into a starchy matrix decreases the global water content with a resultant increase in the cellulose nanofibril content. Typically, the thermal properties are improved and the char yield of composites films increased with the addition of fillers (Wilhelm *et al*., 2003; Huang *et al*., 2004; Cyras *et al*, 2008)

Dynamic Mechanical Thermal Analysis

The thermo-mechanical behavior of rice starch film and rice starch film reinforced with starch nanocrystals was studied using a dynamic mechanical thermal analyzer (DMTA). Figure 4A shows the storage modulus (E') as a function of the temperature of rice starch film and rice starch film reinforced with starch nanocrystals. The storage modulus, related to the composite stiffness when starch nanocrystals was introduced, of the rice starch film increased. For example, the storage modulus of rice starch film containing 30%(w/w) starch nanocrystals presented about 4.58×10^8 MPa which is about 2 times higher than that of the unfilled rice starch film (2.52×10^8 MPa). For temperatures below T$_g$, the composite film is in the glassy state and the storage modulus slightly decreases with temperature. These results agreed with the study conducted by Angellier *et*
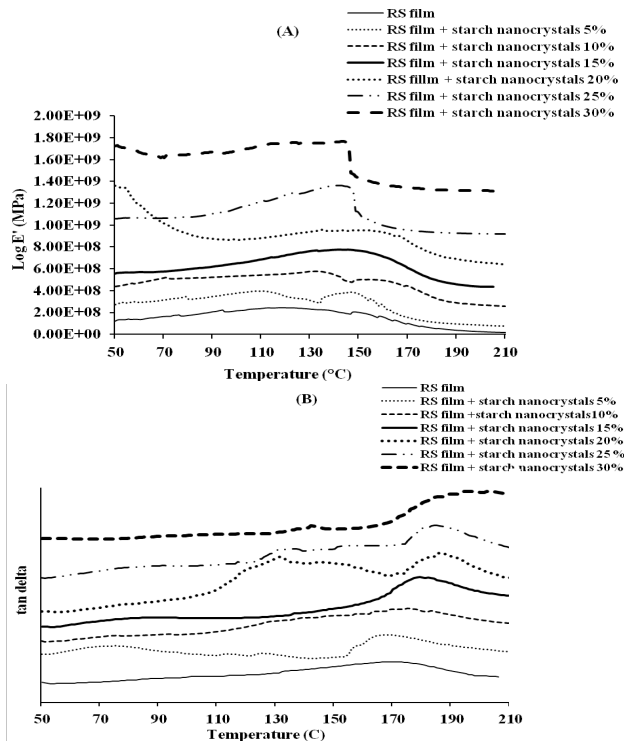
Figure 4. The dynamic mechanical behavior of both (A) storage modulus (E') and (B) loss factor (tan δ) as a function of temperature for for rice starch films and rice starch films reinforced with starch nanocrystals at 5-30%
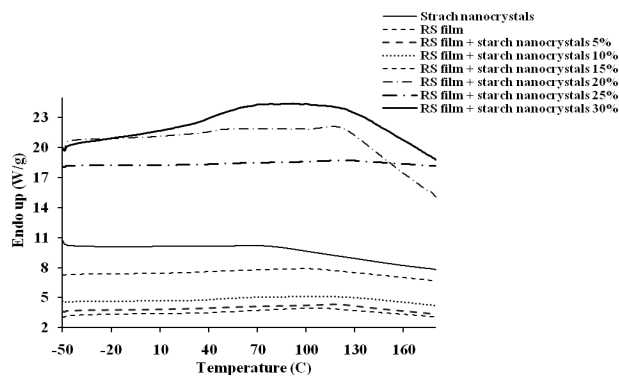

Figure 5. DSC curve of starch nanocrystals, rice starch films and rice starch films reinforced with starch nanocrystals at 5-30%

al. (2005). They found that, for starch nanocrystals reinforced in an acrylic polymer matrix, the storage modulus of composite was increased with increasing starch nanocrystals content compared to the pure acrylic polymer film. This reinforcing effect was similar to the experimental data reported by Kristo and Biliaderis (2007) and Chang *et al.* (2010). These studies dealt with the increase of the storage modulus of starch matrix with increasing concentrations of starch nanocrystals and chitin nano particles, respectively.

Figure 4B shows the tan δ curve of rice starch film and rice starch film reinforced with starch nanocrystals as a function of temperature. Usually the position of the tan δ peak is used as the definition

of glass transition temperature (T_g). The main tan δ peak shifts to a higher temperature as the starch nanocrystals content increases. Thus the T_g (tan δ peak temperature) of rice starch film at about 170°C increased along with an increase in starch nanocrystals content. It reached a maximum point at about 30 wt% of the starch nanocrystals content, thus achieving T_g at about 202°C. The shift of the main relaxation to a higher temperature usually indicates restricted molecular movement. This is because of the strong interactions through hydrogen bonding between the amorphous polymeric matrixes and reinforcing particles. This interfacial H-bonding leads to a strong absorption of polymer chains on the surface of nanoparticles (Smith *et al.*, 2003). Similarly, Chang *et al.* (2010) reported that the T_g of glycerol plasticized-potato starch film shifted to higher temperature with an increase in chitin nanoparticles. This indicated that the chitin nanoparticles improved the intermolecular interaction of glycerol plasticized-potato starch film in the starch-rich phase. This brought adjacent chains of starch close, restraining chain mobility, and reducing the free volume (Yu *et al.*, 2008). In addition, Angellier *et al.* (2006) indicated an increase in the relaxation temperature of thermoplastic waxy maize starch film when adding starch nanocrystals. The increased of T_g may be due to a direct contact between the starch nanocrystals and amylopectin-rich domains. This would confirm the presence of interactions between the filler and the matrixes due to the hydrogen bonding force and starch nanocrystals reducing the mobility of amylopectin chains. Most of the composites exhibited a higher relaxation peak than did the rice starch films. This is attributed to the incorporation of a significant quality in the starch nanocrystals and their elevated degrees of crystallinity, which is in agreement with the results of Liu *et al.* (2010). It was also noted that a double-peak of tan δ for rice starch films containing 20-30% starch nanocrystals was observed, which suggested an aggregation of starch nanocrystals. Aggregations of fillers would result in the heterogeneous collections of polymer matrix and filler (Chang *et al.*, 2010)

Differential Scanning Calorimeter (DSC)

Differential scanning calorimeter (DSC) measurements were performed for all the starch nanocrystals, rice starch films and rice starch films reinforced with starch nanocrystals at 5-30%. All the samples were heated from -50 to 180°C with a heating rate of 20°C/min. The DSC traces are shown in Figure 5. No endothermic peaks were observed in the glass transition temperature (T_g) of the rice starch film. However, this can be observed from the increasing
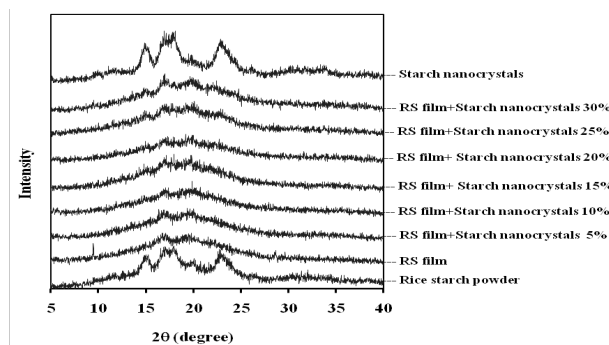
Figure 6. X-ray diffractograms of rice starch powder, starch nanocrystals and rice starch films reinforced with starch nanocrystals at various content
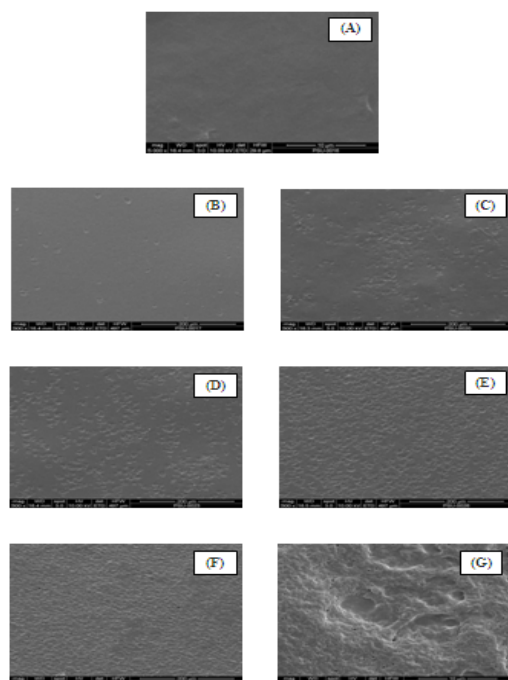

Figure 7. Surface micrographs of rice starch films (A), rice starch films reinforced with 5% (B), 10% (C), 15% (D), 20% (E), 25% (F), 30% (G) of starch nanocrystals

endothermic heat flow when starch nanocrystals is added to rice starch films. With the increase of the starch nanocrystals contents, the endothermic heat flow increased gradually. This was understood by taking into account the concomitant increase in the crystallinity of the starch matrix with filler content. This restricted mobility of amorphous amylopectin chains results from the physical cross-links induced by crystallization (Mathew and Dufrene, 2002). Similarly, Xiong *et al*. (2008) found that the addition of nano-silicon dioxide led to an increase in the thermal stability of starch/polyvinyl alcohol (PVOH) films. This was because the hydrogen bond and chemical bond C-O-Si were generated in nano-silicon dioxide and starch/PVA, which played a role by cross-linking points and restricted the movement of molecular chains. Hence, this resulted in an improved

melting temperature of the composites films. This is in agreement with the results reported by Chen *et al*. (2008) for composites with starch nanocrystals and waterborne polyurethane matrix.

XRD analysis

The XRD patterns of rice starch powder and rice starch nanocrystals are shown in Figure 6. Rice starch powder has a characteristic typical A-type crystalline pattern with strong reflection at 16.8, 18.0 and 22.7°. Following the acid hydrolysis treatment, obvious changes took place in the diffraction pattern of starch nanocrystals. The results showed that the diffraction peaks of the starch nanocrystals were sharper than the diffraction peaks of rice starch powder. A sharper diffraction peak is an indication of a higher crystallinity value in the structure of the starch nanocrystals. The crystallinity values (determined from the peak area of XRD patterns) were estimated as 23.19 and 30.36 for rice starch powder and starch nanocrystals, respectively. During the acid hydrolysis process, acid attacked amorphous areas more rapidly than the crystalline ones (Putaux *et al*., 2003). This process became very sharp, which is associated with an increase in crystalline regions and with losses in amorphous fractions (Punchongkavarin *et al*., 2003). Rice starch films showed an obvious diffraction peak at 16.9° and the crystallinity value was estimated as 13.3%. It decreases to nearly half after gelatinization indicating the destruction of crystalline starch granules during gelatinization (Zhang *et al*., 2007). When adding starch nanocrystals to the films, the results showed that crystallinity was increased. It reached a maximum point at about 20 wt% of the starch nanocrystals content, thus achieving 17.35%. When the starch nanocrystals content exceeded 20 wt%, the crystallinity of the composite film decreased along with an increase in starch nanocrystals content. It was still much higher than unfilled rice starch films. This result was agreement with Yu *et al*. (2008). They reported that when agglomerates of starch nanocrystals formed in the nanocomposite with higher loading-levels of starch nanocrystals, a lower crystalline character of Poly(ε-caprolactone) can be observed. This was when the loading-level of starch nanocrystals was higher than 15 wt%. Its location was in good agreement with the diffraction of the Poly(ε-caprolactone) component, demonstrating the self-aggregation of starch nanocrystals. These results suggest that starch nanocrystals increased the crystallinity of rice starch films, as has been reported by other authors. They have attributed this phenomenon to the more crystalline nature of native starch (Kristo and Biliaderis, 2007; Chen *et al*.,

2008).

Morphology of the films

The morphology of rice starch films and rice starch films reinforced with starch nanocrystals (at 5, 10, 15, 20, 25, and 30%) are shown in Figure 7. It was observed that the surface of rice starch film was smooth (Figure 7A): the rice starch films reinforced with starch nanocrystals became rougher with increased starch nanocrystals content. However, particles of starch nanocrystals in rice starch films were dispersed throughout the composited film matrix of rice starch films reinforced with starch nanocrystals 5 to 20% (Figure 7B and 7E). No obvious aggregations of nanocrystals and microphase separation were observed using scanning electron microscopy (SEM) photographs. In addition, nanopores were also observed throughout the rice starch film reinforced with starch nanocrystals at 25 and 30% (Figure 7F to 7G). This suggested that the high filler films contained nanoporous structures. The nanopores in nanocomposite films were formed due to the aggregation of starch nanocrystals and microphase separation between the nanoparticles and matrix (Chen *et al.*, 2008). That indicated that low filler dispersed more homogenously than high filler in rice starch matrix. This resulted in more chances to interact with rice starch film, thus forming stronger interaction and adhesion on interfaces of filler and matrix (Chen *et al.*, 2008)

Conclusions

Rice starch films reinforced by starch nanocrystals were prepared successfully by casting on leveled trays. The properties of the starch films were improved through the addition of starch nanocrystals. The results showed that the mechanical properties of the film were enhanced by the addition of starch nanocrystals. These indicated that the introduction of starch nanocrystals increased the crystalline peak structure of starch film. The rice starch films containing 20% starch nanocrystals had the best mechanical properties and provided a high tensile strength and elongation at break of about 16.43 MPa and 5.76%, respectively. Furthermore, by increasing the starch nanocrystals content, the water barrier properties of the films were also improved. Increasing endothermic heat flow was observed when addition and increasing of starch nanocrystals and the char yield of rice starch films was enhanced starch nanocrystals increased. Therefore, the addition of starch nanocrystals into rice starch films can improve the thermal stability of rice starch films.

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