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Surface photo-crosslinking of corn starch sheets

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ABSTRACT

Surface of corn starch sheets was modified by cross-linking through ultra violet (UV) irradiation. Sodium benzoate was used as photosensitiser and induced into sheet surface layer by soaking the sheets in the photosensitiser aqueous solution. Photo-crosslinking kinetics was investigated and it was found that the cross-linking reaction at the starch sheet surface was very fast initially (during the first 20 J/cm^2 irradiation), and the irradiation dose was the primary factor to affect the crosslink extent. Afterwards, concentration of photosensitiser aqueous solution became the dominant factor to affect the crosslink extent. The concentration of 0.75% of sodium benzoate aqueous solution gave rise to the highest crosslink extent in the investigated range, 0.1–2.0%. The results of water contact angle measurements and moisture absorption measurements showed that surface photo-crosslinking modifications significantly reduced the hydrophilic character of the starch sheet surface and enhance water resistance of the starch sheets.

1. Introduction

Starch is a natural polymer of D-glucose containing amylose and amylopectin and is found in the majority of plants. Since it is abundant, renewable, inexpensive and biodegradable, starch was considered as one of promising raw materials for developing biodegradable plastics to reduce environmental impact of plastic wastes especially from packaging (Chandra & Rustgi, 1998; Mohanty, Misra, & Hinrichsen, 2000; SinhaRay & Bousmina, 2005). Generally, the native starch granules need to be converted into a homogeneous melt by introducing mechanical and thermal energy under controlled pressure and temperature with presence of water or other plasticizers to disrupt the starch granular structure. The obtained continuous phase of viscous starch melt was known as thermoplastic starch, and it can be processed with existing plastic processing technologies, such as extrusion, injection molding, compressive molding and blow molding, etc. (Lorcks, 1998; Shogren, Fanta, & Doane, 1993).

Thermoplastic starch has found its applications in the plastic market to replace non degradable petrochemical-based products, especially the extruded foamed loose fills (Bastioli, 1998; Tatarka & Cunningham, 1998; Willett & Shogren, 2002). However, one of the major disadvantages of thermoplastic starch, the hydrophilic nature, seriously limits its wider applications. Since thermoplastic starch is sensitive to water, the water content of the materials changes with environmental humidity, this leads mechanical properties of thermoplastic starch changing with ambient humidity during the service and storage.

Numerous studies have been done in an attempt to overcome the hydrophilic nature of thermoplastic starch. Blending thermoplastic starch with biodegradable synthetic polymers is a common method to reduce water sensitivity of thermoplastic starch (Averous, Moro, Dole, & Fringant, 2000; Matzinos, Tserki, Kontoyiannis, & Panayiotou, 2002; Shogren, Lawton, Tiefenbacher, & Chen, 1998; Walia, Lawton, & Shogren, 2002). However, because of lack of compatibility between hydrophilic thermoplastic starch and hydrophobic polymers, the blends usually have poor mechanical properties (Martin & Averous, 2001). Direct grafting of polymeric chains onto the starch backbone could hold starch and synthetic polymer together by chemical bonding so that the two dissimilar polymers could be intimately associated. But, this method gives rise to greater product cost.

Coating water resistant layers at the surface of thermoplastic starch products is another approach to improve water resistance of thermoplastic starch (Andrad, Simao, Thire, & Achete, 2005; Bangyekan, Aht-Ong, & Srikulkit, 2006; Jayasekara, Harding, Bowater, Christie, & Lonergan, 2004; Ryu, Rhim, Roh, & Kim, 2002; Yu & Liu, 2002). This method also needs to solve the problem of poor interfacial adhesion between the surface layer and thermoplastic starch substrate.

It is well known that there are three hydroxyl groups on each of glucose rings in the amylose and amylopectin molecules. These hydroxyl groups are responsible for the hydrophilicity of starch materials. Chemical modification of cross-linking uses reagents having multifunctional groups (cross-linking agents) to react with the hydroxyl groups in starch and create intermolecular bridges so that

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starch molecule networks are formed (Woo & Seib, 1997). By cross-link modifications, easy swelling and gelatinization of native starch are inhibited, cross-linking modified starch granules are even insolvable in boiling water. Cross-linked maize starch has been used to fabricate compression molded specimens and mechanical properties have been investigated (Silva, Ibezim, Ribeiro, Carvalho, & Andrade, 2006). Cross-linking technology has also been applied to modify thermoplastic starch, but few of the works was to modify the extruded thermoplastic starch or their injection molded or compression molded products, most of the cross-linking treatments were applied to starch films prepared by solution casting (Marques et al., 2006; Rioux, Ispas-Szabo, Ait-Kadi, Mateescu, & Juhasz, 2002). A novel technology, photo-crosslinking, has been developed recently to crosslink thermoplastic starch (Delville, Joly, Dole, & Bliard, 2002; Delville, Joly, Dole. P., & Bliard, 2003). This technology uses mixture of starch, plasticizers and sensitizers as feedstock to prepare thermoplastic starch by extrusion processing and converts the extruded thermoplastic starch into films, then applies UV irradiation to crosslink the prepared thermoplastic starch films.

Surface modification of thermoplastic starch is an interesting approach which can change some surface properties of materials without changing their bulk composition and characteristics. By introducing hydrophobic groups to substitute the superficial hydroxyl groups of thermoplastic starch, the hydrophilic character of thermoplastic starch surface was decreased (Bengtsson, Koch, & Gatenholm, 2003; Carvalho, Curvelo, & Gandini, 2005). However, organic solvents were used in these surface modifications, this increases the processing cost and gives rise to environmental and health concerns.

Surface photo-crosslinking provides an option to modify thermoplastic starch surface without using organic solvents. Comparing with the bulk photo-crosslinking, the amounts of sensitizers used in surface photo-crosslinking would be significantly lower, and the cross-linking reaction should be easier in the surface layer. An efficient process of surface photo-crosslinking of thermoplastic starch could have significant application industrially for thermoplastic starch products. In this paper, surface photo-crosslinking modification of corn starch sheets through UV irradiation using sodium benzoate as photosensitiser was investigated and some characterization results for the surface modified sheets were presented.

2. Experimental

2.1. Materials

Corn starch was purchased from Changchun Jincheng Corn Development Co. Ltd., Da Cheng Group (Changchun, China). The photosensitiser, sodium benzoate, was supplied by Tianjin Guangfu Institute of Fine Chemicals (Tianjin, China) and used without further purification. Dimethylsulfoxide (DMSO) was used as a solvent for determining swelling degree and gel mass of surface modified sheets.

2.2. Sheet preparation

Starch sheets were prepared by compressing extrusion cooked corn starch.

A twin-screw co-rotating extruder (CET-35, Coperion Keya (Nanjing) Machinery Co. Ltd., Nanjing, China) with 35.6 mm diameter and a 38 L/D ratio screws was used for the extrusion cooking. The barrel sections 1–6 were maintained at 60, 85, 110, 130, 100, and 80 °C, respectively. The screws were operating at 100 rpm. Starch and water were fed independently by a twin-screw feeder (Coperion Keya (Nanjing) Machinery Co. Ltd., Nanjing, China) and a peristaltic pump (Baoding Longer Precision Pump Co. Ltd., Baoding, China) to give an overall feed rate of 75 g/min and an overall water content of 35% w/w (wet weight basis). A die plate heated to 75 °C was used to form the extrudate into a ribbon with 80 mm width and 10 mm thickness. Once stable extruder operation was achieved, as judged from constant motor current and product output, the extruded ribbons were collected.

A piece of extruded ribbon was put between two polyester sheets and compressed at 80 °C to prepare starch sheets with thickness of about 0.3 mm. After temperature was cooled down to room temperature, the polyester sheets were peeled off, and the starch sheets were dried naturally to moisture content about 12–13% and sealed in zip plastic bags for experimental use.

2.3. Surface photo-crosslinking

The photosensitiser, sodium benzoate, was dissolved in distilled water to prepare photosensitiser aqueous solutions with different concentrations (ranged from 0.1% to 2%). The starch sheets were conditioned at 57% RH for water equilibrium, then cut into small pieces (25 × 20 mm, weighing approximately 0.185 g) and soaked in the photosensitiser aqueous solution for various periods of time. When the sheets were taken out, the excess solution on the surfaces was dripped. The starch sheets containing photosensitiser in surface layer were exposed to ultra violet light at normal atmospheric condition with a UV mini-crosslink machine (Scients03-II, Ningbo Xinzhi Biological Science and Technology Co. Ltd., Ningbo, China). The size of exposure chamber is 34 cm wide, 29.5 cm deep and 15 cm high. There are five parallel tube lamps (28 cm long, 10 W each, emitting at 254 nm) on the top of the chamber. The samples were put at the chamber bottom for irradiating to a desired dose by using the energy (J/cm^2) setting system equipped in the UV mini-crosslink machine. This setting system uses radiometer to measure irradiation dose continuously, and the irradiation stops automatically when the energy dose at the chamber bottom reached the set value.

2.4. Characterization

2.4.1. Swelling degree and gel mass

Determinations of swelling degree (SD) and gel mass (GM) were carried out following the procedure described by Delville, et al., (Delville et al., 2002). The UV irradiated sheets were conditioned at 57% RH for moisture absorption equilibrium then immersed in DMSO in which starch sheet is originally soluble. The insoluble part (swollen sheet) was filtered out, wiped lightly and weighted (the amount was referred to as m_s) in an analytical balance with a precision of 0.1 mg. After that, the insoluble part was first rinsed in water and then in ethanol to remove the DMSO. The insoluble part was dried at 80 °C for 6 h and reconditioned at 57% RH then weighted (the amount was referred to as m_d). The surface area normalized swelling degree and gel mass were calculated by following formulas:

$$\text{Normalized SD} = (m_s - m_d)/(m_d \times A)$$
$$\text{Normalized GM} = m_d/A$$

where A is the surface area of sample sheet for photo-crosslinking modification.

2.4.2. Contact angle measurements

Contact angle measurements were carried out by using a contact angle instrument, Contact Angle System OCA20 (Dataphysics, Germany), and the Sessile and Captive drop method was applied. The samples were conditioned at 57% RH for moisture equilibrium before measurements. A 3 μl droplet of distilled water was placed on the sheet surface. The contact angles were measured on both sides of the drop and averaged. Each reported contact angle was the mean value of at least three measurements taken at different positions on the sample. The measurements were made at room temperature in a closed box.

2.4.3. Stereomicroscopy

A stereomicroscopy, SteREO Discovery V12 (ZEISS, Germany), was used to observe the surface topographies of the control and surface photo-crosslinking modified starch sheets.

2.4.4. Moisture absorption

Moisture absorption was measured by storing the samples at room temperature in desiccators with controlled relative humidities which were maintained by using saturated salt solutions according to standard practices (ASTM E 104-85). The chosen salts were LiCl, $MgCl_2$, NaBr, NaCl, and KNO_3, and the corresponding humidities at room temperature were 11%, 33%, 57%, 75%, and 93% RH. Before putting the sheet samples into desiccators, they were fully dried in an oven at 80 °C and weighted in an analytical balance with a precision of 0.1 mg, then the back surface (the one not facing the UV lamps during irradiation) and the four edges were covered with white vaseline (Tianjin Shuangsheng Chemical Factory, Tianjin, China) to ensure only the UV irradiated surface was exposed to the chosen humidity environment and weighted again. The purpose of Vaseline coatings was to examine how the surfaces with different crosslink extents affect the kinetic of moisture sorption. A set of dried samples were put in a desiccator with a given humidity. After being stored for predetermined periods of time, some of these samples were taken out and weighted to build a moisture sorption kinetic curve. The weighted samples were replaced in the desiccators for the equilibrium measurements. The equilibrium was considered to be reached when the weight gain less than 1% since the last weighting. The moisture content (MC) was calculated using the measured wet weight, W_w, and the dry weight, W_d, by:

$$MC = (W_w - W_d)/W_d$$

3. Results and discussion

3.1. Photo-crosslinking reaction

It is known that the sensitizer, sodium benzoate, would be photo-decomposed under UV irradiation to produce radicals and the cross-linking reaction occurs through a radical mechanism by hydrogen abstraction (Delville et al., 2002; Ghosh & Gangopadhyay, 2000). Investigation of the photo-crosslinking kinetics could provide an efficient route to reach a desired extent of surface modification. The starch macromolecular network formed by UV irradiation can be characterized by the measurements of swelling degree and gel mass (Delville et al., 2002). Surface area normalized gel mass is directly related to the macromolecule's crosslink extent and surface area normalized swelling degree related to the density of the newly created network (Follain, Joly, Dole, & Bliard, 2005). These two values allow the photo-crosslinking kinetics was expressed as a function of UV irradiation energy dose.

Figs. 1 and 2 showed the normalized swelling degree and gel mass as a function of UV irradiation energy dose for the samples soaked in the sodium benzoate aqueous solutions with different concentrations for 90 s, respectively. Basically, for a given concentration of sodium benzoate aqueous solution, the swelling degree decreases and the gel mass increases with increasing of irradiation energy dose. However, the cross-linking reaction at the surface appeared initially to be very fast. It can be seen that during the first 20 J/cm² irradiation dose, swelling degree decreased and gel mass increased rapidly. After this region the curves leveled off and reached a plateau which was less-dependant on the irradiation energy dose.

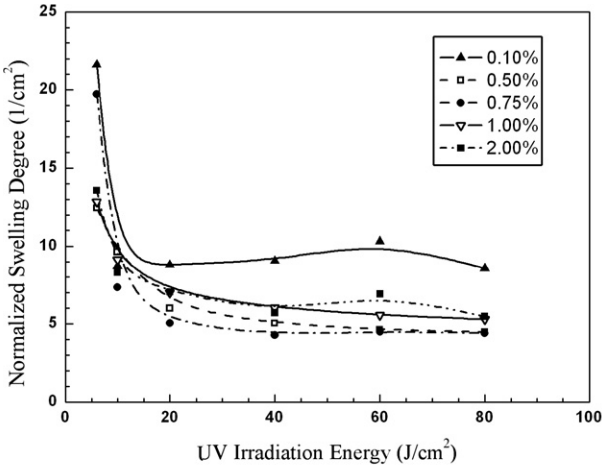

Fig. 1. Changes of normalized swelling degree against UV irradiation energy for the samples soaked in sodium benzoate aqueous solutions with different concentrations for 90 s.

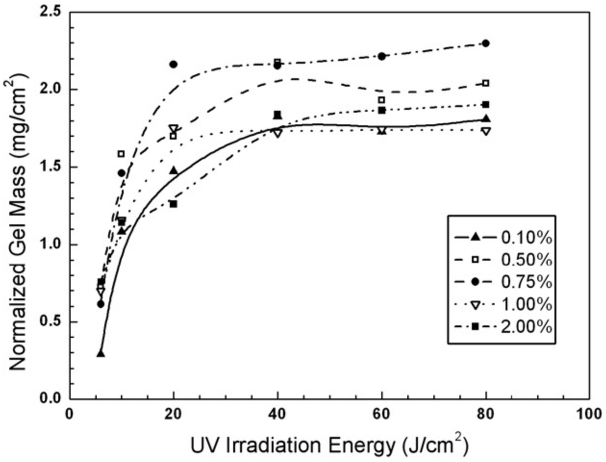

Fig. 2. Changes of normalized gel mass against UV irradiation energy for the samples soaked in sodium benzoate aqueous solutions with different concentrations for 90 s.

It is understandable that the cross-linking reaction at starch sheet surface was initially fast. First, with the progress of crosslink reaction, the formation of the intermolecular bridges due to cross-linking would lead decrease of starch macromolecular mobility which in turn reduces the cross-linking reaction kinetics. On the other hand, since the temperature in the exposure chamber increased slightly during irradiation, some of the water in samples escaped and the samples became drier especially for the high energy dose exposure which could last several hours. The effects of plasticizer (water and glycerol) on the photo-crosslinking of starch sheets have been documented (Delville et al., 2002). High plasticizer content enhances the reaction kinetics, but could reduce the final crosslink extent due to decreasing of the probability of macroradicals combining. The water loss during irradiation decreases starch molecular mobility and would further reduce the cross-linking reaction kinetics.

It was noted that the influence of concentration of photosensitiser aqueous solutions on the initial part of reaction kinetics curves was not marked. However, the concentration of photosensitiser aqueous solutions significantly affects the final plateau values of both normalized SD and normalized GM. For normalized gel mass kinetics, the concentration of 0.1% of photosensitiser aqueous solution gave a lower plateau value of normalized GM, and the plateau value increased with increasing of photosensitiser aqueous solution concentration, i.e. the crosslink extent increased with photosensitiser aqueous solution concentration. However, when photosensitiser aqueous solution concentration was higher than 0.75%, the plateau value of normalized GM decreased with increasing of photosensitiser aqueous solution concentration. For normalized swelling degree kinetics, the situations were similar but reversed, i.e. the plateaus values of normalized SD deceased first, then increased with increasing of photosensitiser aqueous solution concentration, and the concentration of 0.75% gave the minimum plateau value. These results indicated that a concentration of 0.75% of sodium benzoate aqueous solution is sufficient to crosslink the surface layer of starch sheets and no improvements in reaction kinetics and final crosslink extent were observed by further increasing the concentration of photosensitiser aqueous solution in the investigated range. It can be imagined that, for a given soaking time, the higher the concentration of photosensitiser aqueous solution was, the more amount of the photosensitiser would be induced into the surface layer of the starch sheet. An excessive amount of the photosensitiser could increase UV energy absorption and decrease UV penetration depth into the exposed sample, which would give rise to a lower crosslink extent characterized by normalized gel mass.

Fig. 3 showed the normalized swelling degree and gel mass as a function of UV irradiation energy for the samples soaked in 0.75% concentration of sodium benzoate aqueous solution with different periods of time. Basically, the shapes of the kinetics curves for different soaking times were similar and possessed the common feature described in Figs. 1 and 2. It can be seen that 10 s soaking in sodium benzoate aqueous solution gave rise to relative slow reaction kinetics and lower gel mass plateau value compared to 30 and 90 s soakings. However, for samples soaked in sodium benzoate aqueous solution for 30 and 90 s, there was no significant difference in reaction kinetics and normalized gel mass. It was noted that, when determining the gel mass by immersing the irradiated sheets into DMSO, the insoluble part in the sample of 30 s soaking was a thinner but denser film, while the one for the 90 s soaking was relative thicker but looser and floccule-like. These observations suggest that, compared to 30 s soaking in the 0.75% concentration sodium benzoate aqueous solution, there may exist a cross-linking gradient in the modified surface layer for the 90 s soaking sheets under the investigated irradiation conditions. Longer soaking in photosensitiser solution could increase the thickness of surface layer containing the photosensitiser, however, the UV penetration depth is limited for a given system and condition. The contribution of soaking time to the final cross-link extent is dependant on both the concentration of photosensitiser aqueous solution and the UV penetration depth in the system.

3.2. Contact angle

One of the primary aims of surface photo-crosslinking of starch sheets is to investigate how the surface modifications influence the hydrophilic character of the material. Contact angle measurements provide a quantitative characterization of material surface energy. An increase in contact angle with water indicates an enhancement of hydrophobic character of surface and a lower value for the polar component of the surface energy.

Fig. 4 showed the water contact angles of the control sheet and the sample sheets modified by soaking in 0.75% concentration of sodium benzoate aqueous solution for 90 s and exposing under UV irradiation with different energy doses. The results in Fig. 4 showed that the surface photo-crosslinking carried out on the starch sheets gave rise to a significant increase in the value of surface water contact angle. However, it was found that the water contact angle of the surface modified sheets showed a trend of decreasing with increasing of irradiation energy dose (the samples soaked in other concentrations of sodium benzoate aqueous solution had similar results). These results were not expected, because with increase of UV irradiation dose crosslink extent were increased markedly especially for the first 20 J/cm^2 exposure, and more free hydrophilic hydroxyl groups in the surface layer were consumed by the cross-linking reaction. Therefore, the surface hydrophilic character should be reduced with increasing of UV irradiation dose, at least for the first 20 J/cm^2 exposure, and a higher value of water contact angle should be yielded.

Surface contact angle correlates with the surface roughness i.e. the contact angle may change when the surface roughness changes. Surface modification through photo-crosslinking by soaking the starch sheets in photosensitiser aqueous solution and exposing them under UV irradiation with different energy doses may cause the sheets having different surface toughness. Moreover, the surface layer of the starch sheets was subjected to swell-

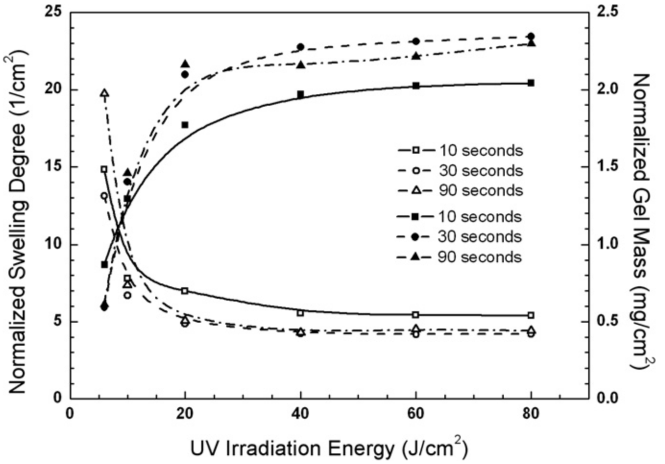

Fig. 3. Changes of normalized swelling degree (open symbol) and gel mass (solid symbol) against UV irradiation energy for the samples soaked in 0.75% concentration of sodium benzoate aqueous solution for different periods of time.

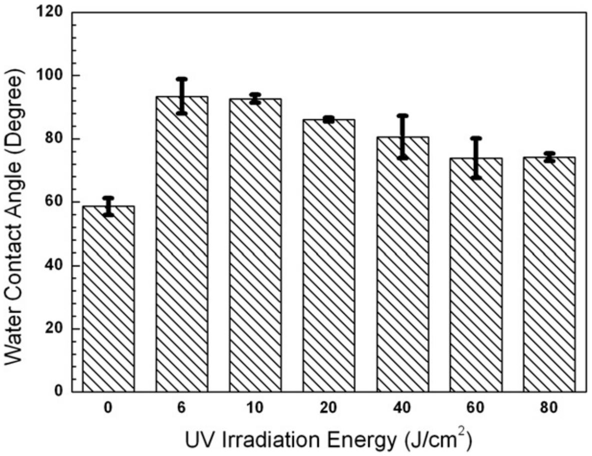

Fig. 4. Water contact angles of the control starch sheet and those soaked in 0.75% concentration of sodium benzoate aqueous solution for 90 s and exposed under UV with different energy doses.

ing, drying and shrinking in the treatment of photo-crosslinking, micro-cracks may form at the surface during this process. All of these could give rise to the water contact angle changing with photo-crosslinking treatment conditions. The surface morphologies of the control and modified sheets were studied with stereomicroscope and the micrographs were shown in Fig. 5. Examining the micrographs in Fig. 5, it can be seen that there was no notable difference in the surface roughness between the control sheet and the surface photo-crosslinking modified sheets and no micro-cracks were observed on the surfaces of modified sheets. These observations suggested that the decrease of water contact angle of modified sheets with UV irradiation energy dose should not be attributed to the surface roughness and possible formation of surface micro-cracks. No attempt was made to further explore the reason causing the water contact angle decrease with UV irradiation dose in this study and it was left for further consideration.

3.3. Moisture absorption and water resistance

As starch is sensitive to moisture, which affects the mechanical properties of thermoplastic starch materials, any improvement in reducing moisture sensitivity and enhancing water resistance of thermoplastic starch materials is highly important. Fig. 6 showed the moisture absorption isotherms at room temperature for the sheets soaked in 0.75% concentration of sodium benzoate aqueous solution for 90 s and exposed under UV irradiation with different energy doses. It can be seen that, after surface modification, the isotherms showed a notable lower moisture uptake than the control one in the common moisture absorption region (30–70% RH). This effect was particularly pronounced in the high RH area. A 17% difference was observed at 93% RH between the modified one with 80 J/cm^2 UV exposure and control one. Moisture absorption kinetics was examined at 93% RH, the data were presented in Fig. 7. Basically, moisture absorption was quick in the first 10 h conditioning, afterwards the curves turned into level. The influence of surface photo-crosslinking modification on the initial part of moisture absorption kinetics curves was not marked. However, Fig. 7 clearly showed that the equilibrium moisture content in the modified sheets decreased with UV irradiation energy. The results in Fig. 7 suggested that at 93% RH, although surface photo-crosslinking modification did not give rise to a marked change of moisture absorption rate of starch sheet, it did reduce the moisture uptake ability of the starch sheets.

In order to exam the enhancement of water resistance of the starch sheet after surface photo-crosslinking modification, both of the control and surface modified sheets were put into hot water kept at 90 °C by a heating plate for comparison. It was found that the control one swelled very fast and lost its integrity and turned into fragments in about 8 min while the sheets modified by surface

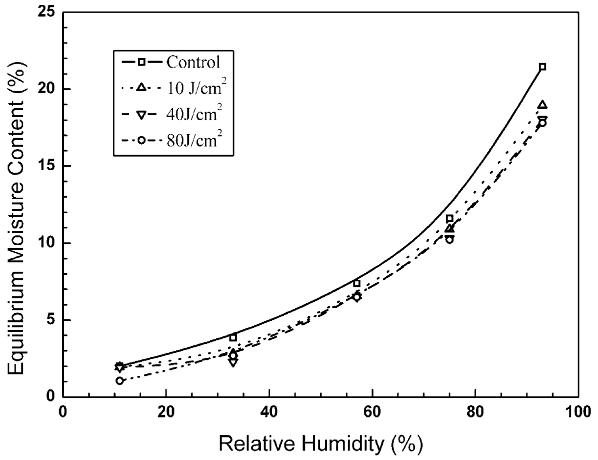

Fig. 6. Moisture absorption isotherms at RT of the control sheet and those soaked in 0.75% concentration of sodium benzoate aqueous solution for 90 s and exposed under UV with different energy doses.

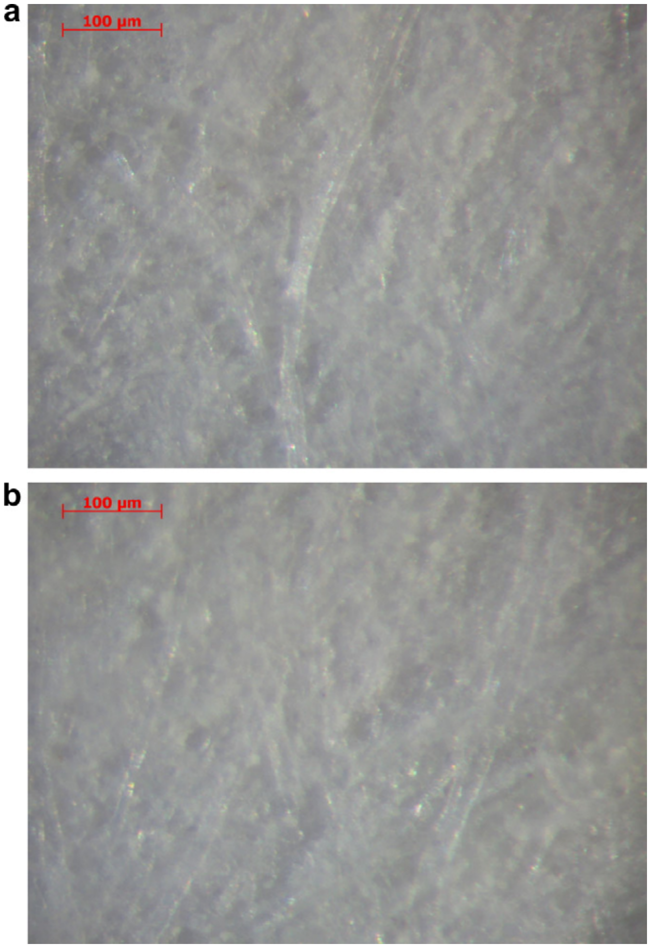

Fig. 5. Stereomicroscopy micrographs of the starch sheet surface, (a) Control, (b) Soaked in 0.75% concentration of sodium benzoate aqueous solution for 90 s and exposed under UV with 80 J/cm^2.

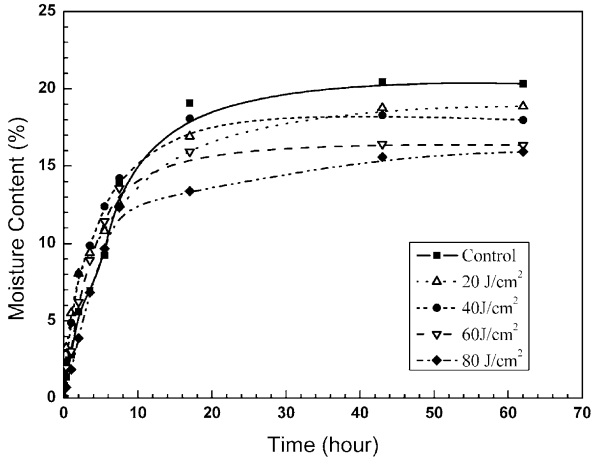

Fig. 7. Moisture absorption kinetics at RT and 93% RH for control sheet and those soaked in 0.75% concentration of sodium benzoate aqueous solution for 90 s and exposed under UV with different energy doses.

photo-crosslinking could last longer time to remain intact although handling the sheets picked up from the hot water it was apparent that they deform at very lower stresses. For the sheets soaked in 0.75% concentration of sodium benzoate aqueous solution for 90 s and exposed under UV irradiation with 10, 40, and 80 J/cm^2, the times that the sheets remained their integrity in the 90 °C water were about 32, 55, and 67 min, respectively. These observations indicated that surface modification through photo-crosslinking does dramatically enhance the water resistance of corn starch sheet, and this technology may further widen the possible application area of thermoplastic starch materials.

4. Conclusions

Surface of corn starch sheets can be modified by cross-linking under ultra violet (UV) irradiation by using sodium benzoate as photosensitiser and inducing it into the sheet surface layer through soaking the sheets in the photosensitiser aqueous solution. Photocrosslinking kinetics investigations showed that the cross-linking reaction at the surface of samples was very fast initially, and the irradiation dose was the primary factor to affect the crosslink extent in the first 20 J/cm^2 irradiation dose. Beyond this range, the concentration of photosensitiser aqueous solution became the dominant factor to affect the crosslink extent. The concentration of 0.75% of sodium benzoate aqueous solution gave rise to the highest crosslink extent in the investigated range, 0.1–2.0%. Results of measurements of water contact angle and moisture absorption showed that surface photo-crosslinking treatments significantly reduced the hydrophilic character of the starch sheet surface and enhance the water resistance of the starch sheets. The surface photo-crosslinking technology may provide a novel approach to change the surface properties of thermoplastic starch products and widen the possible application of these kinds of materials.

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