



Preparation and characterization of surface crosslinked TPS/PVA blend films

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ABSTRACT

Surface crosslinked thermoplastic starch (TPS)/PVA blend films were prepared by applying ultra violet (UV) irradiation. Sodium benzoate was used as photosensitizer and induced onto film surface layer by soaking the TPS/PVA films in the photosensitizer aqueous solution. The effects of concentration of photosensitizer aqueous solution, soaking time and UV irradiation dose on the surface photocrosslinking reaction were investigated. Physical properties, such as water contact angle, moisture absorption, swelling degree and solubility in water as well as mechanical properties of the films were measured to characterize the influence of the surface photocrosslinking modification. The obtained results showed that the surface modification considerably reduced the surface hydrophilic character of the TPS/PVA films, enhanced the film's water resistance and also increased tensile strength and Young's modulus but decreased elongation at break of the films.

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1. Introduction

In the last two decades, there has been an increasing interest in developing biodegradable polymers and products from renewable resources to reduce environmental impact of plastic waste (Chandra & Rustgi, 1998; Mohanty, Misra, & Hinrichsen, 2000; Yu, Dean, & Li, 2006). Considerable effort has been made to develop and modify thermoplastic starch (TPS) due to its biodegradability, renewability and low cost. Although TPS has found its applications in the plastic market to replace non degradable petrochemical-based products, such as the extruded foamed loose fills (Bastoli, 1998; Tatarka & Cunningham, 1998; Willett & Shogren, 2002), the hydrophilic nature and poor mechanical properties of TPS seriously limit its extensive applications.

Blending TPS with biodegradable synthetic polymers is a common method to improve mechanical properties and reduce water sensitivity of TPS. Poly(vinyl alcohol) (PVA), a biodegradable and water soluble polymer, has been widely used to blend with starch for better mechanical properties because of its flexibility and good film forming capability (Chen, Cao, Chang, & Huneault, 2008; Jayasekara, Harding, Bowater, Christie, & Lonergan, 2004; Lawton, 1996; Shogren, Lawton, Tiefenbacher, & Chen, 1998; Siddaramaiah, Raj, & Somashekar, 2004; Yoon, Chough, & Park, 2006a; Zhou et al., 2006). Blends of TPS/PVA have been studied as one of the most popular biodegradable polymers.

Starch granules consist of linear amylose and highly branched amylopectin molecules. The hydroxyl groups on glucose rings in

amylose and amylopectin molecules are responsible for the hydrophilicity of TPS. Although PVA can improve mechanical properties of TPS materials, PVA is also sensitive to water because it contains a number of hydroxyl groups in itself, which renders TPS/PVA blends unsuitable for many high humidity applications.

Crosslinking technologies have been used to modify TPS or starch/PVA blend systems in order to improve their physical and mechanical properties. Crosslinking agents, such as epichlorohydrin (Kim, Na, Park, Yoon, & Ihm, 2002; Sreedhar, Chattopadhyay, Karunakar, & Sastry, 2006), boric acid (Yin, Li, Liu, & Li, 2005), borax (Sreedhar, Sairam, Chattopadhyay, Syamala Rathnam, & MohanRao, 2005), glutaraldehyde (Pal, Banthia, & Majumdar, 2008; Ramaraj, 2007; Yoon, Chough, & Park, 2006b) and tetraethylene glycol diacrylate (Marques et al., 2006), were used to react with the hydroxyl groups in starch to create intermolecular linkages so that macromolecular networks were formed. These crosslinking agents were usually added into aqueous solution of starch/PVA mixture and then the crosslinked films were prepared by casting method. Gamma irradiation was also applied to treat casting solutions to prepare crosslinked starch/PVA films (Kim, Jo, Park, & Byun, 2008). Post-treatments through irradiation of electron beam (Zhai, Yoshii, & Kume, 2003) and ultraviolet (UV) (Delville, Joly, Dole, & Bliard, 2002; Follain, Joly, Dole, & Bliard, 2005; Khan, Bhattacharia, Kader, & Bahari, 2006) were used to crosslink the extruded or compression molded TPS/PVA films or sheets. For the UV photocrosslinking, photosensitizers or photoinitiators were generally needed to be incorporated into the materials during processing to produce reactive radicals that initiate subsequent crosslinking reactions under UV irradiation.

Comparing with the bulk crosslinking, surface crosslinking modification of TPS based materials provides an approach to

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reduce surface hydrophilic characteristics of the materials without changing their bulk composition. The amounts of crosslinking agents or photosensitizers used in a surface modification would be significantly lower compared to a modification of bulk material. Author's previous work (Zhou, Zhang, Ma, & Tong, 2008) showed that the surface photocrosslinking of gelatinized corn starch sheets, through soaking the sheets in photosensitizer aqueous solution and then exposing them under UV irradiation, reduced the sheet surface hydrophilicity and improved water resistance of the sheet. Sodium benzoate, a preservative widely used in foods and cosmetics, was used as the photosensitizer.

Since PVA contains a number of hydroxyl groups, and it was demonstrated that PVA can be photocrosslinked under UV irradiation when using sodium benzoate as sensitizer (Follain et al., 2005; Takakura, Takayama, & Ukida, 1965). Therefore, it is worthy to apply the surface photocrosslinking modification method (Zhou et al., 2008) in TPS/PVA blend system to improve physical properties of the blend. In this paper, surface photocrosslinked TPS/PVA films were prepared and some physical and mechanical properties of films were characterized to investigate the effects of the surface modifications.

2. Experimental

2.1. Materials

The corn starch was supplied by Changchun Jincheng Corn Development Co. Ltd., Da Cheng Group (China). Poly(vinyl alcohol) (PVA) with polymerization degree of 1750 ± 50 was purchased from Shenyang Dongxing Reagent Factory (China). The photosensitizer, sodium benzoate, was obtained from Tianjin Guangfu Institute of Fine Chemicals (China). All these materials were used as received without further purification. Dimethylsulfoxide (DMSO), from Tianjin Dodi Chemical Industry Co. Ltd. (China), was used as a solvent for determining swelling degree and gel mass of surface modified films.

2.2. Film preparation

Films were fabricated by solution casting method. The composition of 70% corn starch, 15% PVA and 15% glycerol was chosen in this study. First, PVA solution was prepared by dissolving 7.5 g PVA in 500 g distilled water through heating at 95 °C by a water bath. Then, 35 g dry starch and 7.5 g glycerol were mixed and dispersed in 500 g distilled water to make a suspension. The temperature of the starch slurry was slowly raised to 95 °C with stirring and the PVA solution was added. The mixture was kept at 95 °C and maintained stirring for 60 min to gelatinise the starch. The volume of the slurry was maintained by adding water during this period. The mixture was removed from heat and was distributed in desired amount into PMMA trays for casting and dried at 60 °C. The prepared films with thickness of about 0.22 mm were peeled from the trays and sealed in zip plastic bags for experimental use.

2.3. Surface photocrosslinking modification

The photosensitizer aqueous solutions with different concentrations were prepared by dissolving sodium benzoate in distilled water. After conditioned at 57% RH to moisture equilibrium, small pieces (25 mm × 20 mm) of the TPS/PVA film were soaked in the photosensitizer aqueous solutions for various periods of time. When the films were taken out, the excess solution on the surfaces was absorbed by using filter papers. The films containing sodium benzoate in surface layer were then exposed to UV light at normal atmospheric condition for surface crosslinking modification. A UV

mini-crosslink machine (Scients03-II, Ningbo Xinzhi Biological Science and Technology Co. Ltd., China) was used for UV exposure. 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 (J/cm^2). The UV irradiation dose was controlled by using the energy setting system equipped in the UV mini-crosslink machine. This energy 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. Degree of crosslinking

The degree of crosslinking was characterized by measuring the film's gel mass (GM) and swelling degree (SD) in DMSO. Determinations of GM and SD were carried out following the procedure described in literature (Delville et al., 2002) but with minor modifications. The UV irradiated films were immersed in DMSO in which the TPS/PVA blend film is originally completely soluble. After 24 h, the insoluble part (swollen film) was filtered out and weighed (the amount was referred to as m_s) in an analytical balance with a precision of 0.1 mg. Afterwards, 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 weighed (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 for photocrosslinking 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). A droplet of distilled water (3 μl) was placed on the film 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 10 measurements taken at different positions on the film. All the samples were conditioned at 57% RH for moisture equilibrium before measurements.

2.4.3. Stereomicroscopy

A stereomicroscopy, SteREO Discovery V12 (Zeiss, Germany), was used to observe the surface topographies of the control and surface crosslinked TPS/PVA films.

2.4.4. Moisture absorption

Moisture absorption was measured by storing the samples at room temperature in desiccators with controlled relative humidities (11%, 33%, 57%, 75% and 93% RH) which were maintained by saturated salt solutions (Zhou et al., 2008). Briefly, the films were fully dried and weighed, then the back surface (the one not facing the UV lamps during irradiation) and the four edges of the sample films 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 weighed again. The film samples with white vaseline coatings were replaced in the desiccators for the moisture absorption measurements. The moisture content (MC) was calculated using the measured wet weight, W_w , and the dry weight, W_d , by:

$$\text{MC} = (W_w - W_d) / W_d$$

The moisture equilibrium was considered to be reached when the weight gain less than 1% since the last weighing.

2.4.5. Swelling degree and solubility in water

Control and surface modified films were dried and weighed, and then they were immersed in distilled water for 24 h and swollen sufficiently. After the removal of the excess surface water, the swollen films were weighed and the swelling degree was calculated as the ratio of the weight of distilled water absorbed to the weight of the dried film. After the swollen films were fully dried in an oven at 80 °C, the weight of dried films was measured and the solubility was calculated as the ratio of the weight of the dissolved portion to the weight of the dried film.

2.4.6. Mechanical properties

The specimens, 50 mm long dumbbells with 4 mm neck width, were cut from the prepared films. After surface photocrosslinking modifications, all the specimens were conditioned at 57% RH and room temperature to the equilibrium. The tensile tests were carried out by using an Instron Universal testing Machine model 1121 (Instron, USA) at a crosshead rate of 10 mm/min. Tensile strength, Young's modulus and elongation at break were obtained. At least five specimens were measured for each experimental condition and the average values were taken.

3. Results and discussion

3.1. Surface photocrosslinking reaction

The macromolecular network of starch–starch, starch–PVA and PVA–PVA created by UV irradiation can be characterized by the GM and SD in DMSO (Follain et al., 2005; Zhou et al., 2008). The surface area normalized GM is directly related to the mass of TPS and PVA macromolecules involved in the crosslinking network and the surface area normalized SD related to the crosslinking density of the newly created network.

Author's previous work (Zhou et al., 2008) demonstrated that, for the surface crosslinked gelatinized corn starch sheets, the 0.75% sodium benzoate aqueous solution gave rise to the highest degree of crosslinking (characterized by higher GM and lower SD) in the investigated sodium benzoate aqueous solution concentration range, from 0.1% to 2.0%. Therefore, the concentration of sodium benzoate aqueous solution varying from 0.5% to 1.0% was chosen in this study.

Fig. 1 showed the normalized GM and normalized SD as a function of UV irradiation dose for the TPS/PVA films soaked in sodium benzoate aqueous solutions with different concentrations for 30 s. In a given soaking time, the concentration of photosensitizer aqueous solution affects the sensitizer content in the surface layer of TPS/PVA films. Basically, for the three studied concentrations, GM increased and SD decreased rapidly in the first 20 J/cm² UV irradiation. Afterwards, both GM and SD curves gradually turned into level. These results indicated that the surface photocrosslinking reaction appeared initially to be fast and then slowed down for all the investigated concentrations. The intermolecular linkages created by UV irradiation lead to decrease of macromolecular mobility, and this is the main reason for the decline of crosslinking reaction speed.

From Fig. 1, it can be seen that the concentration of photosensitizer aqueous solutions influenced both kinetics and final value of the normalized GM and SD. When UV irradiation dose was higher than 20 J/cm², the 0.75% sodium benzoate aqueous solution gave rise to a higher GM compared to the concentrations of 0.5% and 1.0%. This indicated that more TPS and PVA molecular chains were involved in the formation of the macromolecular network when using 0.75% sodium benzoate aqueous solution. As shown in

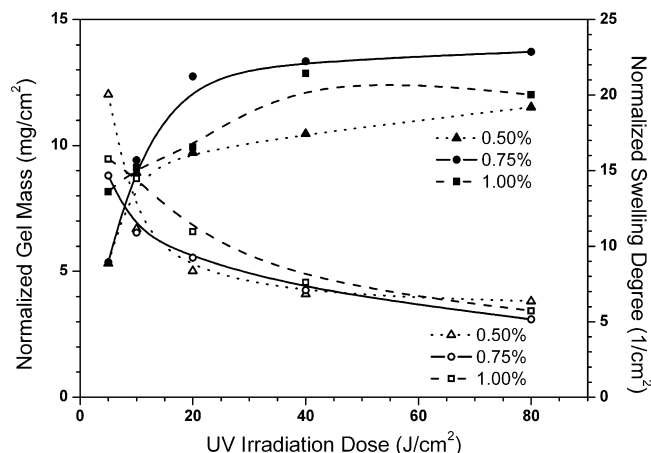


Fig. 1. Changes of normalized gel mass (solid symbol) and swelling degree (open symbol) against UV irradiation dose for the TPS/PVA films soaked in sodium benzoate aqueous solutions with different concentrations for 30 s.

Fig. 1, a higher concentration of sodium benzoate aqueous solution seemed to cause a slower kinetics of the normalized SD, but the difference in the final value of normalized SD was not noticeable. These suggested that the effect of concentration of sodium benzoate aqueous solution on crosslinking density in the crosslinked surface layer was not considerable especially under higher dose UV exposure (larger 40 J/cm²).

A higher concentration of photosensitizer aqueous solution would result in higher photosensitizer content in the surface layer. An excessive amount of the photosensitizer could increase UV energy absorption and decrease UV penetration depth into the exposed sample, which would lead to a lower degree of crosslinking characterized by normalized GM. The results presented in Fig. 1 indicated that the 0.75% sodium benzoate aqueous solution is more efficient than the others to crosslink the surface layer of the TPS/PVA films, i.e., it gave rise to higher GM and lower SD with faster kinetics. Although there may exist an optimum concentration around 0.75% which could crosslink the TPS and PVA molecules more efficiently, no further investigations were made to explore it.

Fig. 2 showed the normalized GM and normalized SD as a function of UV irradiation dose for the films soaked in 0.75% sodium

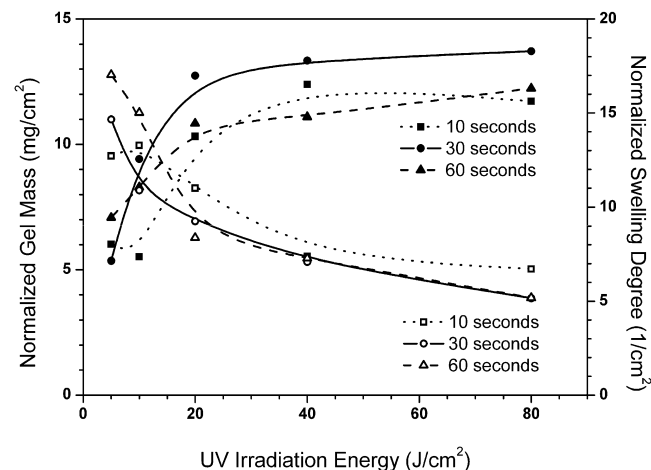


Fig. 2. Changes of normalized gel mass (solid symbol) and swelling degree (open symbol) against UV irradiation dose for the TPS/PVA films soaked in 0.75% sodium benzoate aqueous solution for different periods of time.

benzoate aqueous solution with different periods of time. The soaking time of a sample in photosensitizer aqueous solution determines the thickness of the surface layer containing photosensitizer which in turn affects the depth range that macromolecular network can be formed. Basically, the GM and SD kinetic curves for different soaking times were similar and possessed the common feature described in Fig. 1. From Fig. 2, it can be seen that the 30 s soaking gave rise to higher GM value and lower SD value with faster kinetics compared to the other investigated soaking times.

The effect of soaking time on the normalized GM and normalized SD is complicated. Generally, shorter soaking resulted in a thinner surface layer containing the photosensitizer, which could lead to a lower GM value because less TPS and PVA macromolecules would be involved in the crosslink reaction. On the other hand, since the photosensitizer in the surface layer has a gradient distribution along the depth, therefore, different soaking time could also lead to the photosensitizer content in the surface layer be different even the concentration of photosensitizer aqueous solution is the same. Longer soaking could result in not only a thicker surface layer containing photosensitizer but also higher photosensitizer content in the surface layer if the concentration of photosensitizer aqueous solution is high enough. The effect of soaking time on the degree of crosslinking characterized by normalized GM and normalized SD is dependant on the concentration of photosensitizer aqueous solution, the UV irradiation dose and the UV penetration depth in the system, while the UV penetration depth is influenced by photosensitizer content in the surface layer of the system.

Comparing the results of surface photocrosslinking reaction of the TPS/PVA films with that of the surface crosslinked corn starch sheets (Zhou et al., 2008), it was found that addition of PVA significantly increased the final values of normalized GM (about five times). However, incorporation of PVA did not considerably change the final values of normalized SD, although the SD kinetics was slowed down especially under high UV irradiation doses.

3.2. Water contact angle

It should be pointed out that the two surfaces of the TPS/PVA films prepared by casting method have different morphologies. The surface contacting with PMMA plate during the film formation was obviously smoother than the surface contacting with air. The measured water contact angles for the air contact surface and PMMA contact surface were 77.67 ± 1.71 and 80.67 ± 1.37 , respectively. It is known that surface contact angle correlates with the surface roughness and increases as the surface roughness increases. The higher water contact angle at the smoother PMMA contact surface can not be explained by the difference in surface roughness. A possible reason for the difference in water contact angle at the two surfaces is that the PMMA plate may affect orientation of the polar hydroxyl groups at the PMMA contact surface. Compared to air, it may be more difficult for the hydroxyl groups in TPS and PVA to orient to PMMA at the surface. An increase in water contact angle indicates an enhancement of hydrophobic character of surface and a lower value for the polar component of the surface energy.

Since the TPS/PVA films curved towards the PMMA contact surface after soaking in photosensitizer aqueous solution, the air contact surface was selected to face the UV lamps so that the films could be spread out and stuck on bottom of the exposure chamber for photocrosslinking. Thus, all the values of water contact angle for the surface crosslinked films were measured at the air contact surface. Fig. 3 presented the water contact angles of the control film (air contact surface) and the surface crosslinked films prepared by soaking the films in 0.75% sodium benzoate aqueous solu-

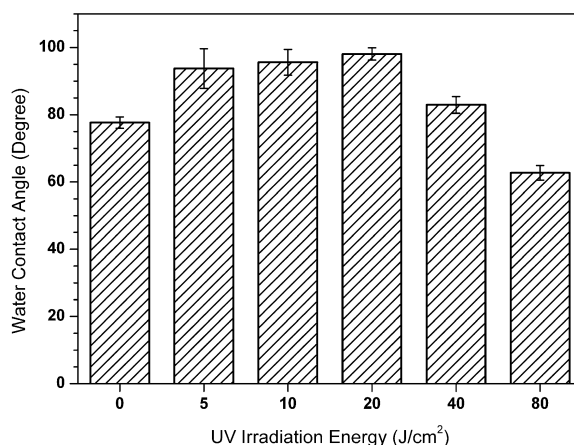


Fig. 3. Water contact angles of the control film (air contact surface) and the surface crosslinked films prepared by soaking in 0.75% sodium benzoate aqueous solution for 30 s and exposing under different UV doses.

tion for 30 s and irradiated with different UV doses. It can be seen that, after surface photocrosslinking modifications, water contact angle of the TPS/PVA films jumped up significantly and continuously increased with increasing of UV irradiation dose until 20 J/cm^2 . Afterwards, the water contact angle showed a trend of declining and decreased to a value below that of the control one when irradiation dose reached 80 J/cm^2 . The increase of water contact angle with UV irradiation dose can be explained as follows: with progress of crosslinking reaction, more and more hydroxyl groups in the surface layer, either on TPS or PVA molecular chains, have been consumed and these hydroxyl groups are never available to water. However, the decline of water contact angle when the films were further irradiated with UV can not be explained by the consumption of water bonding sites. The phenomenon that water contact angle decreased with UV irradiation dose was also observed in the surface photocrosslinked corn starch sheets (Zhou et al., 2008).

It can be imagined that, during the described surface photocrosslinking modification, the film surface layer was subjected to swelling, drying and shrinking. The treatments may cause surface toughness change and induce micro-cracks at the surface. The surface morphologies of the control and surface crosslinked films were examined by a stereomicroscope (the pictures were not shown). There were no observable micro-cracks on the surfaces of the surface crosslinked films. Therefore, the decrease of water contact angle with UV irradiation dose for the surface crosslinked films should not be attributed to possible formation of surface micro-cracks. The stereomicroscope observations of the surface roughness for the surface crosslinked films could not give significantly scientific information to lead to a conclusion that a high dose UV irradiation resulted in change of the surface roughness. Atomic force microscope (AFM), confocal laser scanning microscopy (CLSM), attenuated total reflectance FT/IR spectra (ATR-FT/IR) and X-ray photoelectron spectroscopy (XPS) have been considered for characterizing the surface roughness and hydroxyl groups at the surface of the crosslinked films. Further work is under investigation.

3.3. Moisture absorption

The equilibrium moisture contents of the control film and the surface crosslinked films prepared by soaking the films in 0.75% sodium benzoate aqueous solution for 30 s and exposing under different UV doses were measured in various humidities at room temperature, the results were shown in Fig. 4. It can be seen that, after surface modification, the films showed a notable lower mois-

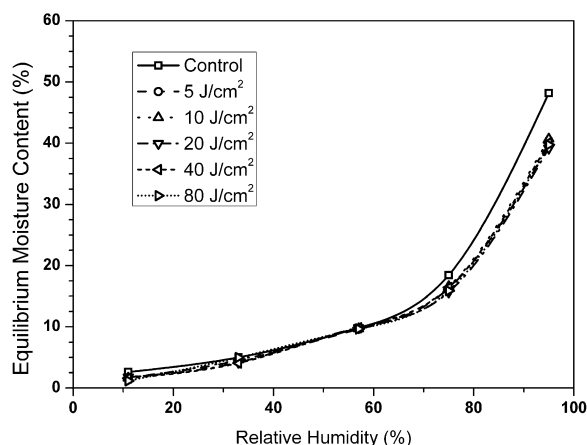


Fig. 4. Moisture absorption isotherms at RT of the control film and those soaked in 0.75% sodium benzoate aqueous solution for 30 s and exposed under different UV doses.

ture uptake than the control one in the high RH range, although this effect was negligible in the common humidity region (40–70% RH). At 93% RH, the equilibrium moisture content of the film modified with 80 J/cm² UV irradiation dose decreased about 18% compared to that of the control one.

Moisture absorption kinetics of the films were examined at 93% RH, the data were presented in Fig. 5. Basically, for all the control and surface crosslinked films, moisture absorption were quick in the first 10 h conditioning, afterwards the curves gradually turned into level. The influence of surface crosslinking modification on the initial part of moisture absorption kinetic curves was not marked. However, the final values of moisture uptake for the surface crosslinked films decreased. These results suggested that although surface UV photocrosslinking modification did not give the TPS/PVA films a noticeable change in moisture absorption rate, it did dramatically reduce the moisture uptake ability of the films.

Fig. 6 showed swelling degree in water and solubility of the control and surface crosslinked TPS/PVA films. It can be seen that, as the UV irradiation dose increased, both swelling degree in water and solubility decreased. Generally, in a crosslinked structure, the crosslinking points restrict the molecular mobility of the polymer chains. Since the crosslinking density (the number of crosslinking points) in surface layer increased with UV irradiation dose, the expansion of the surface layer and the solubility of TPS and PVA

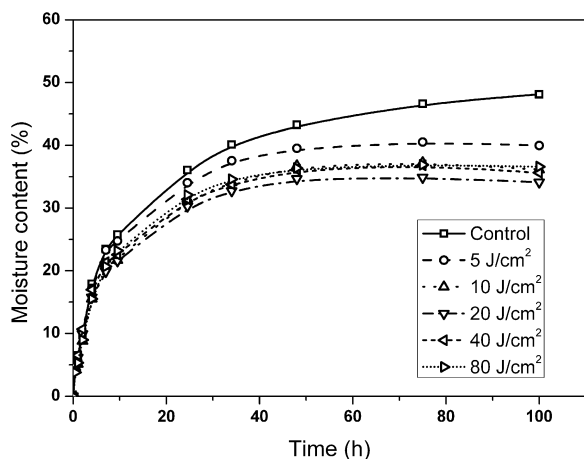


Fig. 5. Moisture absorption kinetics at RT and 93% RH of the control film and those soaked in 0.75% sodium benzoate aqueous solution for 30 s and exposed under different UV doses.

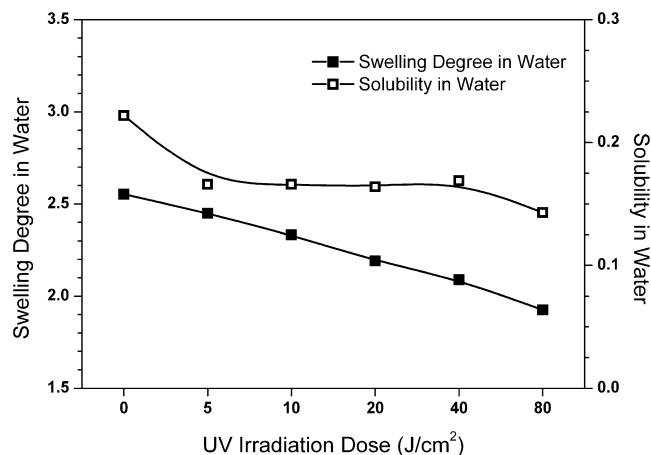


Fig. 6. Effects of surface photocrosslinking modification on the swelling degree and solubility in water of the TPS/PVA films.

were reduced as the UV irradiation dose increased. In other words, the surface photocrosslinking modification enhanced water resistance of the TPS/PVA blend films. It was noted that, after 24 h soaking in water, the control film still kept flat, and the film irradiated with 5 J/cm² UV dose just curled towards the crosslinked surface (the one facing the UV lamps during irradiation), while the other films irradiated with higher UV doses totally rolled up towards the crosslinked surface. These phenomena suggested that the two surfaces of the modified films had different swelling behaviors, which meant the macromolecular structures were different in the two surface layers of the crosslinked films. The above observations indicated that either the photocrosslinking created macromolecular network only existed in the UV irradiated surface layer or the crosslinking density in the films had a gradient distribution along the thickness direction.

3.4. Mechanical properties

Mechanical properties are important criterion for many practical applications of materials. In order to investigate the influence of surface photocrosslinking modification, the mechanical properties of the surface crosslinked TPS/PVA films were measured and compared to the control one.

Fig. 7 presented the tensile strength and elongation at break of the control film and the surface crosslinked ones measured at room

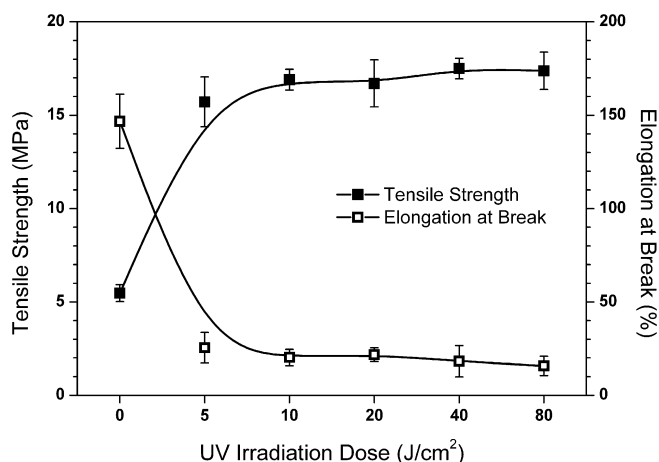


Fig. 7. Effects of surface photocrosslinking modification on tensile strength and elongation at break of the TPS/PVA films.

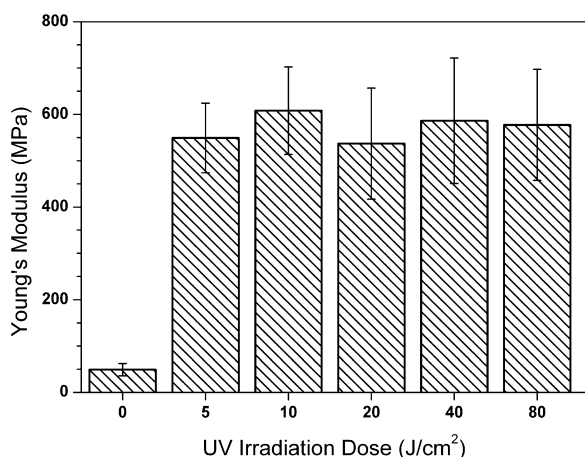


Fig. 8. Effects of surface photocrosslinking modification on Young's modulus of the TPS/PVA films.

temperature and 57% RH. The surface crosslinked films were prepared by soaking the films in 0.75% sodium benzoate aqueous solution for 30 s and exposing under different UV irradiation doses. Compared to the control film, surface photocrosslinking modification significantly increased tensile strength and decreased elongation at break of the TPS/PVA films. It was observed that the tensile strength of the crosslinked films irradiated with 5 J/cm² dose enhanced 2.87 times compared with the control one. Moreover, the tensile strength of surface crosslinked films increased with UV irradiation dose, but the changes were not considerable. Compared to the crosslinked films irradiated with 5 J/cm² dose, 80 J/cm² irradiation only yielded about 10% increase of tensile strength. The effect of surface photocrosslinking on the elongation at break was dramatically. The surface crosslinking modification with 5 J/cm² irradiation dose caused about 83% decline of the elongation at break, and the elongation at break continuously decreased with increasing of irradiation dose. The elongation at break dropped 89% after 80 J/cm² irradiation. Fig. 8 showed the Young's modulus of the control film and the surface crosslinked ones measured at room temperature and 57% RH. The surface photocrosslinking modification significantly increased the Young's modulus of the TPS/PVA films, but the effect of UV irradiation doses was not marked. The Young's modulus of the surface crosslinked TPS/PVA films was increased at least 11 times after modification.

It is known that the mechanical properties of TPS based materials change with the moisture content. Although surface photocrosslinking reduced the equilibrium moisture content in the TPS/PVA films at higher relative humidities, the equilibrium moisture contents in the control film and the surface crosslinked ones were almost same at 57% RH as shown in Fig. 4. Therefore, the difference in mechanical properties between the control and the modified films shown in Figs. 7 and 8 was mainly due to the presence of the crosslinked surface layer. As demonstrated before, the crosslinking density of the starch and PVA macromolecular chains in the surface layer increased with increasing of UV irradiation dose. Theoretically, an increase of crosslinking density of macromolecular chains would lead to increasing of tensile strength and Young's modulus as well as decreasing of elongation at break of polymers. Therefore, the results presented in Figs. 7 and 8 were expected.

4. Conclusions

The surface of TPS/PVA blend films was crosslinked by soaking the films in sodium benzoate aqueous solution and exposing them under UV irradiation. In the range of the investigated surface modification conditions, soaking in 0.75% sodium benzoate aqueous

solution for 30 s gave rise to a most efficient surface photocrosslinking in the TPS/PVA films, i.e., yielded a highest degree of surface crosslinking characterized by higher gel mass and lower swelling degree with a faster kinetics. Characterizations of physical properties, such as water contact angle, moisture absorption, swelling degree and solubility in water showed that the surface photocrosslinking modification significantly reduced the surface hydrophilic character of the TPS/PVA films and enhanced the water resistance of the films. The results of mechanical properties measurements showed that the surface photocrosslinking modification increased tensile strength and Young's modulus but decreased elongation at break of the TPS/PVA films.

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